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# THE USE OF AMINES AS EXTRACTANTS FOR URANIUM FROM ACIDIC SULFATE LIQUORS: A PRELIMINARY REPORT

K. B. Brown
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## ABSTRACT

Over 100 different organonitrogen compounds have been examined for their ability to extract uranium from aqueous solutions, particularly sulfate solutions, of the types usually encountered in uranium ore processing. The more promising of these have been examined further with respect to other characteristics essential to practical application, especially selectivity for uranium, reagent loss to the aqueous phase, compatibility with practicable diluents, maintenance of adequate extraction power over a range of liquor compositions, and compatibility with practicable stripping methods. Most of the compounds originally considered have been found worthy of only cursory examination. The important outcome on the other hand is that several compounds, specifically several long chain secondary and tertiary amines have been identified as having considerable promise for practicable solvent extraction application.

# I. INTRODUCTION

The investigation and evaluation of new reagents for the separation of uranium from various aqueous systems by solvent extraction methods have been underway for some time at this laboratory. Progress reports have been issued periodically covering work with organophosphorus compounds as well as a wide variety of other acidic, basic, neutral and amphoteric reagents.(1) Since early 1952, a portion of this general program has been devoted to a fairly intensive study of organonitrogen compounds, particularly the simple amines. This report is intended to be the first in a series of reports covering the results from these studies.

Prior to the work reported here, British investigators(2) had found that strong inorganic and organic acids could be simply and efficiently removed from aqueous systems by extracting with chloroform, benzene or toluene solutions of certain amines, a chloroform solution of methyldioctylamine being the best of those tested for this particular purpose. The British work was primarily concerned with the development of a method for the separation of strong and weak acids, but it was also suggested that the acidified amine solutions might find other uses as liquid anion exchangers, e.g., "in the recovery of metals, such as chromium or vanadium, after oxidation to anions." Sometime later, further tests of the amines were made by F. L. Moore of the Oak Ridge National Laboratory Analytical Division to determine the general applicability of these reagents to analytical separation problems.(3) Using solutions of methyldioctylamine in chloroform, Moore confirmed the British work and, in addition, was able to demonstrate the extraction of polonium, plutonyl and uranyl from acid solutions, the separation of niobium from tantalum, protactinium from thorium, tin from antimony, and cobalt from nickel and chromium.

In this laboratory the studies of the amines (and other organonitrogen compounds) have been almost entirely concerned with the possible practical application of these reagents to the large scale extraction and separation of uranium from aqueous solutions which may also contain a large variety of other ions. Because of the frequent use of sulfuric acid in

uranium raw material processing, most of the extraction studies have been made on uranium-bearing sulfate solutions, in some cases "pure," and in other cases containing appreciable amounts of those contaminants which are often dissolved from an ore during leaching, e.g., iron, aluminum, phosphate, fluoride, etc. Extractions from nitrate, chloride, and phosphate solutions have also been studied, but only briefly and with comparatively less success. More extended studies of these systems are planned for the future.

For purposes of discussion, the work with the amines as conducted at this laboratory may be divided into three categories: (a) screening tests aimed at the discovery and selection of reagents most likely to be useful in practicable application, (b) process development studies, and (c) studies of the fundamental factors which govern the extraction of acids and of uranium.

Thus far over 100 different reagents have been examined in the screening tests including simple primary, secondary and tertiary amines, quaternary ammonium salts, polyamines and other organonitrogen compounds. With such a wide choice of compounds, it is obvious that detailed examinations of each would be prohibitively time consuming. Consequently, in the work which will be described, a systematic approach to the problem has been used in which those reagents showing the least promise have been eliminated in a stepwise manner. In initial experiments, for example, each reagent has been tested for its ability to form extractable uranium complexes from aqueous solutions of the general type most likely to be encountered in process operations. The most acceptable reagents from these tests were next examined in regard to their ability to meet other specifications of importance to a successful solvent extraction process, e.g., compatibility with practicable solvents, acceptably low loss to the aqueous phase through solubility, sufficient selectivity for uranium, adequate extraction coefficients over a range of solution composition, compatibility with practicable stripping methods, etc. By conducting such experiments in sequence, those compounds which "failed" in one series of tests were eliminated from at least intensive consideration in a subsequent series.

Logically following the screening program were studies wherein the more likely reagents were examined in greater detail from a process development viewpoint. Here, countercurrent as well as single-stage tests, with actual (or synthetic) leach liquors, were directed toward a closer evaluation of operational characteristics, reagent usage,

and insofar as possible the optimum process schemes for the extraction and stripping cycles. Numerous studies of this type have been completed and with favorable results. Only portions of these data will be given here, however, since full presentation of the combined screening and development work is much too cumbersome for a single document. A separate report including the process development studies is being prepared and will be issued later.

Fundamental studies of the amine extractions have been started only recently, and at the time of this writing are only partially complete; hence, only tentative conclusions from very preliminary results can be presented here. It is expected that other reports on the fundamental, screening, and development aspects of the program will be issued when sufficient additional data have been accumulated.

## II. DESCRIPTION OF COMPOUNDS

Most of the organonitrogen compounds discussed in this report were obtained from commercial sources such as the Armour Chemical Division of Armour and Company, Carbide and Carbon Chemicals Company, Eastman Kodak, Rohm and Haas, etc. Many other compounds, particularly the long chain secondary and tertiary amines, were prepared at this laboratory, and still others were obtained from chemical specialty houses such as the Bios Laboratories, Edcan Laboratories, and A. D. Mackay, Inc. The methods followed in syntheses of compounds at this laboratory are given in Appendix B and descriptive information concerning all of the compounds tested may be found in Appendix A. The name, source (manufacturer or vendor), molecular weight, structure, purity level, and type of impurities present have been tabulated insofar as this information is available.

Since the organonitrogen compounds contain many types of impurities both similar and dissimilar to the major component, the reagent purity is a property difficult to determine by direct measurement and difficult to describe in specific terms. Reasonable approximations of the "purity levels" of most of the compounds examined here have been obtained, however, by relying upon several sources of information, as for example, equivalent weight determination by non-aqueous titration, carbon-hydrogen-nitrogen analyses, distillation ranges, manufacturer's data, solubility measurements, etc. On the basis of such information the compounds, exclusive of mixtures, listed in Appendix A may be grouped very approximately as follows: 90-95% (purity level) for most of the secondary and tertiary amines prepared at this laboratory, 80-90% for amines from chemical companies and specialty houses, and 70-95% for the quaternary salts, polyamines and other miscellaneous nitrogen compounds. The nature and distribution of impurities found in the various reagents are dependent upon several factors such as the type of compound prepared, the purity of the starting materials and the preparation path. Common contaminants to be expected are unreacted starting materials, water, alcohols, and other organonitrogen compounds of the same or a different class. Some of these compounds could react with uranium in a manner analogous to that of the major component whereas others would be essentially inert in the extraction process.

It is apparent from the foregoing that the reagents available were ordinarily not of a suitable grade for

physicochemical measurements. They have, however, been generally acceptable for the screening studies reported here since these were concerned with relatively large differences of performance between different reagents. It has not been necessary in either the screening or the process development studies to interpret measurements wherein the differences were small. (Special batches of high-purity di-n-decylamine were prepared for use in the fundamental studies; cf. Appendix C.)

# III. EXPERIMENTAL

## A. PRELIMINARY URANIUM EXTRACTION TESTS

A preliminary evaluation of the organonitrogen compounds has been made by subjecting each of the reagents in question to a simple series of extraction tests. In the initial tests, an acidic uranyl sulfate solution, U = 1 gm/l, $SO_4^=$ = 1M, pH ~1, has been contacted in a separatory funnel with equal volumes of the following reagent-diluent mixtures: (a) 0.1M reagent in chloroform, (b) 0.1M reagent in benzene, and (c) 0.1M reagent in benzene, prewashed with an acid sulfate solution. After five minutes of vigorous shaking, the organic and aqueous layers were separated and the extractions were measured by fluorometric determination of the uranium in each phase.

When the extractions with (c) were significantly less than those with (b), it was assumed that the compounds were appreciably soluble in aqueous solutions and interest in these particular reagents diminished. In cases where loss by aqueous solubility was not evident with 0.1M reagent, and the reagent showed sufficient extraction to be of interest, the tests were repeated using 0.01M reagent as more sensitive to solubility loss. (The latter tests served only to amplify the solubility losses; they were not particularly useful for comparisons of the extraction power of different reagents, since the organic phase at this low reagent concentration was frequently approaching saturation with uranium.)

The results from the preliminary tests made thus far are given in Table 1. Since more than 100 different compounds have been examined, this table is quite long and, at first glance, formidable. Consequently, for simplicity of presentation, the more important observations and conclusions which may be drawn from the data are presented in an itemized fashion below.

### Primary Amines

1. The straight chain primary amines gave moderate extractions of uranium into chloroform but were ineffective

Table 1

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

A. Primary Amines

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,5,5-Trimethylhexyl | 0.1 | 1.0 | 1.2 | 3rd Phase | | 1.1 | 3rd Phase | | 0.9 | nil | nil | Emulsions |
| Armeen 10D | 0.1 | 1.0 | 1.0 | 79 | 4 | 1.0 | --- | --- | 0.9 | nil | nil | Poor |
| Armeen 12D | 0.1 | 1.0 | 1.0 | 43 | 1 | 1.0 | nil | nil | 0.9 | nil | nil | Poor |
| Armeen CD | 0.1 | 0.9 | 1.1 | 76 | 3 | 1.0 | nil | nil | 0.9 | nil | nil | Emulsions w/benzene |
| Armeen 14D (Redistilled) | 0.1 | 1.0 | 0.8 | 7 | <.1 | 1.1 | nil | nil | 0.9 | nil | nil | Poor |
| Armeen 16D (Redistilled) | 0.1 | 1.0 | 1.2 | 3 | <.1 | 0.8 | nil | nil | 1.1 | nil | nil | Emulsion w/benzene |
| Armeen TD | 0.1 | 0.9 | --- | 66 | 2 | --- | 4 | <.1 | 0.8 | <1 | <.1 | Emulsion in aqueous |
| Armeen HTD | 0.1 | 0.9 | --- | Emulsion | | --- | Emulsion | | 0.9 | <1 | <.1 | Poor |
| Armeen SD | 0.1 | 0.9 | 1.0 | 62 | 2 | --- | 2 | <.1 | 0.9 | <1 | <.1 | Emulsions in aqueous |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

A. Primary Amines (Cont'd.)

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Armeen 18D (Redistilled) | 0.1 | 1.0 | 0.8 | 2 | <.1 | --- | nil | nil | 0.9 | nil | nil | Emulsions |
| Cyclohexyl-methyl | 0.1 | 1.1 | 1.3 | 10 | < 1 | 1.5 | nil | nil | 1.2 | nil | nil | Good |
| C&CCC 21F75 | 0.1 | 0.9 | 1.1 | 89 | 8 | 1.1 | --- | --- | 0.9 | --- | --- | Very Poor |
| C&CCC 16F65 (1-isobutyl-3,5 dimethyl hexyl) | 0.01 | 0.9 | 0.9 | 12 | - | 1.0 | 11 | --- | 0.9 | 5 | --- | Good |
| | 0.1 | 0.9 | 1.1 | 97 | 35 | 1.1 | 87 | 7 | 0.9 | 76 | 3 | |
| C&CCC 21F79 (1-isobutyl octyl) | 0.01 | 0.9 | 0.9 | 16 | - | 1.0 | 25 | --- | 0.9 | 22 | --- | Good |
| | 0.1 | 0.9 | 1.1 | 98 | 50 | 1.1 | 95 | 20 | 0.9 | 92 | 12 | |
| C&CCC 21F81 (1(3,ethyl pentyl) 4,ethyl octyl amine (Batch A) | 0.02 | 1.1 | 1.2 | 62 | - | 1.2 | 57 | --- | 1.1 | 58 | --- | Good |
| | 0.1 | 1.0 | 1.1 | 98 | 45 | 1.1 | 98 | 45 | 1.0 | 97 | 35 | |
| | 0.2 | 1.0 | 1.2 | 100 | 300 | 1.2 | 99 | 130 | 0.9 | 98 | 40 | |
| Primene 81T | 0.01 | 1.1 | 1.2 | 24 | - | 1.2 | 1 | --- | 1.1 | 1 | --- | Good |
| | 0.1 | 1.0 | 1.0 | 98 | 60 | 1.0 | 77 | 4 | 0.9 | 69 | 2 | |
| Primene JMT | 0.01 | 1.1 | 1.2 | 39 | - | 1.2 | 39 | --- | 1.2 | 32 | --- | Good |
| | 0.1 | 1.0 | 1.0 | 99 | 90 | 1.1 | 92 | 10 | 0.8 | 89 | 8 | |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

B. Secondary Amines

| Amine | Conc.** | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyllauryl | 0.1 | 1.0 | 1.0 | 85 | 6 | --- | 0.2 | <.1 | 1.0 | *nil | nil | Poor in Benzene |
| Di-n-heptyl | 0.1 | 1.0 | 1.1 | 99 | 100 | --- | 80 | 4 | --- | 2 | <.1 | Poor in Benzene |
| Di-n-octyl | 0.01 | 0.9 | --- | 24 | --- | 1.0 | 40 | --- | 1.0 | * 3 | --- | Poor in |
| (Batch A) | 0.1 | 0.9 | 1.1 | >99 | 120 | 1.1 | 84 | 5 | --- | Emulsion | | Benzene |
| Armeen 2-8 | 0.01 | 0.9 | 0.9 | 21 | --- | 0.9 | 39 | --- | 0.9 | * 2 | --- | Poor in |
| (Batch A) | 0.1 | 0.9 | 1.1 | >99 | 160 | 1.2 | 81 | 4 | --- | Emulsion | | Benzene |
| Di-n-decyl | 0.01 | 0.9 | --- | --- | --- | 0.9 | 39 | --- | 0.9 | * 41 | --- | Good |
| (Batch A) | 0.1 | 0.9 | 1.1 | >99 | 150 | 1.1 | 99 | 90 | 0.9 | * 98 | 60 | |
| Dilauryl | 0.01 | 1.0 | 1.0 | 21 | --- | --- | 35 | --- | 0.9 | * 38 | --- | Good |
| (Batch A) | 0.1 | 1.0 | 1.1 | 99 | 100 | 1.1 | 99 | 80 | 0.8 | * 98 | 60 | |
| Armeen 2-12 | 0.01 | 0.9 | 1.0 | --- | --- | 1.0 | 41 | --- | 0.9 | * 39 | --- | Good |
| (Batch A) | 0.1 | 0.9 | 1.1 | >99 | 300 | 1.1 | 99 | 100 | --- | Emulsion | | |
| Di-n-tetradecyl | 0.01 | 1.0 | --- | 28 | --- | --- | 32 | --- | 0.9 | * 32 | --- | Good |
| (Batch L82) | 0.05 | 1.0 | --- | 95 | 20 | 1.1 | 96 | 20 | 1.0 | * 95 | 20 | |
| Di-n-hexadecyl | 0.01 | 1.0 | --- | 30 | --- | --- | 29 | --- | 0.9 | * 30 | --- | Good |
| (Batch L78) | 0.05 | 1.0 | 1.1 | 97 | 30 | --- | 96 | 20 | --- | * 95 | 20 | |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

B. Secondary Amines (Cont'd.)

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Di-n-octadecyl (Batch L81) | 0.01 | 0.9 | --- | 14 | --- | --- | 15 | --- | 0.9 | *10 | --- | --- |
| Armeen 2C | 0.01 | 0.9 | 1.0 | 22 | --- | 0.9 | 25 | --- | 0.9 | 37 | --- | Good |
| | 0.1 | 1.1 | --- | >99 | 190 | --- | >99 | 160 | 0.9 | 99 | 85 | |
| Armeen 2C Distillation Fractions: | | | | | | | | | | | | |
| 160-180°C, 3mm | 0.3 | 0.9 | 1.1 | 89 | 8 | 1.0 | 79 | 4 | 1.0 | 90 | 9 | Poor |
| 180-200°C, 3mm | 0.3 | 0.9 | 1.0 | 77 | 3 | 1.0 | 89 | 8 | 1.0 | 66 | 2 | Fair |
| 168-184°C, < 1mm | 0.3 | 0.9 | 1.0 | 88 | 8 | 1.0 | 90 | 9 | 1.0 | 48 | 1 | Good |
| 184-200°C, < 1mm | 0.2 | 0.9 | --- | 58 | 1 | --- | 72 | 3 | 0.8 | *73 | 3 | Good |
| Armeen 2HT | 0.05 | 0.9 | 1.0 | 92 | 12 | --- | Insol. | | --- | Insol. | | Good |
| Dicyclohexyl | 0.1 | 1.0 | 1.1 | 38 | < 1 | 1.2 | nil | nil | 1.0 | nil | nil | Good |
| C&CCC 25F25 Di (2 methyl cyclo hexane) methylamine | 0.1 | 0.9 | 1.1 | 96 | 25 | 1.1 | 97 | 40 | 0.9 | nil | nil | Good |
| C&CCC 17F22 Bis (3,3,5,5 Tetramethyl Cyclohexyl) Di 2 ethyl hexyl amine | 0.2 | 1.0 | 1.2 | Ppt. | | 1.2 | Ppt. | | 0.9 | < 1 | < .1 | Good |
| Di(2-ethylhexyl) (Batch A) | 0.01 | 1.0 | --- | 7 | --- | --- | 37 | --- | 0.9 | *12 | --- | Good |
| | 0.1 | 1.0 | 1.1 | 96 | 25 | 1.1 | 99 | 100 | 0.9 | 98 | 40 | |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

B. Secondary Amines (Cont'd.)

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethylhexyl-2-pentylnonyl | 0.01 | 0.9 | 0.9 | 10 | --- | 0.9 | 15 | --- | 0.9 | *16 | --- | Good |
| | 0.1 | 0.9 | 1.0 | 56 | 1 | 1.0 | 91 | 10 | 1.0 | *89 | 15 | |
| C&CCC 15F53 (Batch A) Di(1-isobutyl isoamyl)amine | 0.01 | 1.1 | 1.1 | 9 | --- | 1.1 | 35 | --- | 1.1 | 24 | --- | Good |
| | 0.2 | 1.0 | 1.2 | 91 | 10 | 1.3 | 99 | 75 | 0.9 | 97 | 30 | |
| C&CCC 16F27 isobutyl-3,5 dimethyl hexyl | 0.01 | 1.1 | 1.2 | 2 | --- | 1.1 | 16 | --- | 1.1 | 15 | --- | Good |
| | 0.14 | 1.0 | 1.1 | 48 | 1 | 1.1 | 91 | 10 | 0.9 | 90 | 10 | |
| n-Tetradecyl(3-phenylpropyl) | 0.01 | 1.0 | --- | 45 | --- | --- | 37 | --- | 0.9 | *38 | --- | Good |
| | 0.1 | 0.9 | 1.0 | >99 | 250 | 1.0 | 99 | 75 | 0.9 | *99 | 77 | |
| N-(2-ethylhexyl)-α-methylbenzyl | 0.01 | 1.1 | 1.2 | 36 | --- | 1.1 | 40 | --- | 1.1 | 2 | --- | Good |
| | 0.2 | 1.0 | 1.3 | >99 | 185 | 1.3 | 99 | 70 | 0.9 | 99 | 90 | |
| N-(2-ethylhexyl)-α-xylylbenzyl | 0.015 | 1.1 | 1.2 | < 1 | --- | 1.2 | nil | nil | 1.1 | < 1 | nil | Good |
| | 0.15 | 1.0 | 1.0 | 56 | 1 | 1.0 | 86 | 6 | 0.8 | 85 | 6 | |
| n-Butylaniline | 0.1 | 1.0 | --- | nil | nil | --- | nil | nil | 1.0 | nil | nil | Good |
| p,p'-Dioctyldiphenyl | 0.1 | 1.1 | --- | < 1 | nil | --- | < 1 | nil | --- | < 1 | nil | Good |
| Dibenzyl | 0.1 | 1.0 | 1.1 | 76 | 3 | 1.1 | --- | --- | 0.9 | nil | nil | Poor in $CHCl_3$ |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

C. Tertiary Amines

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N,N-Dimethyl-(2-ethylhexyl) | 0.1 | 1.0 | 1.1 | nil | nil | 1.1 | nil | nil | 1.0 | nil | nil | Good |
| Primene 81T-dimethyl | 0.1 | 1.0 | 1.1 | --- | --- | 1.0 | 1 | <.1 | 0.9 | 1 | <.1 | Good |
| Dimethyl-n-octadecyl | 0.1 | 1.0 | --- | Emulsion | | --- | Emulsion | | --- | Emulsion | | Emulsion |
| Dimethyllauryl (Batch A) | 0.01 | 1.0 | --- | 35 | --- | --- | --- | --- | --- | --- | --- | ---- |
| | 0.1 | 1.0 | 1.1 | 87 | 7 | 1.2 | 1 | <.1 | 0.9 | 1 | <.1 | V. Poor |
| Diethyllauryl | 0.01 | 1.0 | --- | 22 | --- | --- | --- | --- | --- | --- | --- | ---- |
| | 0.1 | 1.0 | 1.1 | 95 | 20 | 1.1 | nil | nil | 0.9 | nil | nil | Fair |
| Dibutyllauryl (Batch A) | 0.01 | 1.0 | --- | 12 | --- | --- | 51 | --- | 0.9 | *52 | --- | ---- |
| | 0.1 | 1.0 | 1.1 | 91 | 10 | 1.1 | 99 | 95 | 1.0 | *98 | 65 | Good |
| Dihexyllauryl (Batch A) | 0.01 | 1.0 | 1.1 | 7 | --- | 1.1 | 48 | --- | 1.1 | *46 | --- | ---- |
| | 0.1 | 1.0 | 1.2 | 85 | 6 | --- | 99 | 110 | 1.1 | *99 | 95 | Good |
| Di(2-ethylhexyl)-lauryl (Batch A) | 0.1 | 1.0 | --- | 16 | <1 | --- | 7 | <.1 | --- | *10 | <1 | Good |
| Bis(β-hydroxy-ethyl)lauryl | 0.1 | 1.0 | 1.1 | 34 | <1 | --- | nil | nil | 1.0 | *--- | --- | ---- |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

C. Tertiary Amines (Cont'd.)

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyldi-n-octyl (Redistilled) (Batch A) | 0.01 | 1.0 | --- | --- | --- | 1.0 | 49 | --- | 0.9 | 45 | --- | ---- |
| | 0.1 | 1.0 | 1.0 | 97 | 30 | 1.1 | 97 | 30 | 0.9 | 95 | 20 | Good |
| N-Methyldi(2-ethylhexyl) (Batch A) | 0.1 | 1.0 | 1.1 | 81 | 4 | 1.1 | 60 | 2 | 0.9 | 23 | < 1 | Good |
| | 0.1 | 1.1 | 1.2 | 89 | 8 | 1.2 | 74 | 3 | 1.0 | 40 | 1 | Good |
| (Batch B) | 0.2 | 1.0 | 1.3 | 91 | 10 | 1.2 | 81 | 4 | 0.9 | 23 | <1 | Good |
| Methyldi-n-decyl (Batch A) | 0.01 | 0.9 | 0.9 | 25 | --- | 0.9 | 49 | --- | 0.9 | 50 | --- | ---- |
| | 0.1 | 1.0 | 1.0 | 98 | 45 | 1.0 | 98 | 45 | 0.9 | 98 | 40 | Good |
| Methyldilauryl (Batch A) | 0.01 | 1.0 | 1.1 | 29 | --- | 1.1 | 61 | --- | 1.1 | *57 | --- | Poor |
| | 0.1 | 1.0 | 1.2 | 98 | 40 | 1.2 | 99 | 70 | 1.1 | 98 | 50 | ---- |
| ß-Hydroxyethyl-dilauryl | 0.1 | 1.0 | 1.1 | 63 | 2 | --- | 84 | 5 | 1.0 | *81 | 4 | Good |
| Methyldi-n-octadecyl | 0.01 | 1.0 | --- | 7 | --- | --- | 52 | --- | 1.1 | *48 | --- | Good |
| Propyldi-n-decyl (Batch A) | 0.01 | 1.0 | --- | 30 | --- | --- | 40 | --- | 0.9 | *42 | --- | ---- |
| | 0.1 | 0.9 | 1.1 | 99 | 150 | 1.0 | 99 | 80 | 0.9 | 99 | 71 | Good |
| Tri-n-butyl | 0.1 | 1.0 | 1.1 | 75 | 3 | 1.1 | 1 | < .1 | 1.0 | .1 | <.1 | Good |
| Tri-n-hexyl | 0.01 | 1.1 | 1.1 | 7 | --- | 1.1 | 46 | --- | 1.1 | 36 | --- | ---- |
| | 0.1 | 1.0 | 1.1 | 75 | 3 | --- | 99 | >100 | 0.9 | 97 | 95 | Good |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

C. Tertiary Amines (Cont'd.)

| Amine | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tri-n-octyl | 0.01 | 1.0 | --- | 5 | --- | --- | 40 | --- | --- | *43 | --- | ---- |
| (Batch G) | 0.1 | 1.0 | --- | 76 | 3 | --- | 99 | 110 | --- | *99 | 95 | Good |
| Tri(2-ethylhexyl) | 0.1 | 1.0 | 1.0 | 4 | <.1 | --- | 16 | < 1 | 1.0 | * 1 | <.1 | Good |
| Tri-n-decyl | 0.01 | 1.0 | 1.1 | 45 | --- | 1.1 | 37 | --- | 1.1 | *39 | --- | ---- |
| (Batch B) | 0.1 | 1.0 | 1.2 | 86 | 6 | 1.2 | 98 | 50 | 1.1 | *98 | 25 | Good |
| Trilauryl | 0.01 | 1.0 | 1.0 | 6 | --- | 0.9 | 46 | --- | 0.9 | *46 | --- | |
| (Batch A) | 0.1 | 1.0 | 1.1 | 80 | 4 | 1.1 | 99 | 140 | 1.0 | *99 | 125 | |
| Dimethylbenzyl | 0.1 | 1.0 | 1.1 | nil | nil | 1.0 | nil | nil | 0.9 | nil | nil | Good |
| Tribenzyl | 0.1 | 1.0 | --- | 1 | <.1 | 1.2 | 1 | <.1 | 1.1 | nil | nil | Good |
| Diethylnaphthyl | 0.1 | 1.0 | --- | nil | nil | --- | nil | nil | 0.9 | *nil | nil | Good |
| Di-n-butylaniline | 0.1 | 1.0 | --- | nil | nil | --- | nil | nil | 1.0 | *nil | nil | Good |
| Ethylbenzyl-aniline | 0.1 | 1.0 | --- | nil | nil | --- | nil | nil | 0.9 | *nil | nil | Good |
| Ethomeen S-15 | 0.1 | 1.0 | --- | 57 | 1 | 1.1 | nil | nil | 1.0 | *nil | nil | Poor |
| Ethomeen S-60 | 0.1 | 1.0 | 1.0 | 79 | 4 | 1.2 | nil | nil | 1.2 | *nil | nil | Fair. Cloudy Phases |
| Ethomeen C-15 | 0.1 | 1.0 | 1.2 | 2 | <.1 | 1.0 | nil | nil | 0.9 | *nil | nil | Fair. Cloudy Phases |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Quaternary Ammonium Compounds

| Compound | Conc.** M | Init. Aq. pH | Chloroform | | | Benzene | | | Benzene (Prewashed)* | | | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Final pH | Extn. % | $E_a^o$ | Final pH | Extn. % | $E_a^o$ | Final pH | Extn. % | $E_a^o$ | |
| Arquad 2C | 0.1 | 1.0 | 1.0 | 43 | 1 | 1.0 | 38 | < 1 | 0.9 | 36 | < 1 | Poor |
| Arquad 2HT | 0.07 | 1.0 | --- | 33 | < 1 | --- | 27 | < 1 | 0.9 | 4 | < .1 | Poor |
| Arquad S | 0.08 | 1.0 | --- | 23 | < 1 | --- | Insol. | | --- | Insol. | | Poor |
| Laurylpyridinium chloride | 0.1 | 1.0 | 1.0 | nil | nil | --- | Insol. | | --- | Insol. | | Poor |
| Roccal | 0.1 | 1.1 | --- | 82 | 5 | --- | 3rd Phase | | 1.4 | 3 | < .1 | Good |
| Cetylpyridinium chloride | 0.1 | 1.0 | --- | 35 | < 1 | --- | Insol. | | --- | Insol. | | Emulsion in Aqueous |
| Cetyltrimethyl-ammonium bromide | 0.1 | 1.0 | --- | 20 | < 1 | --- | Insol. | | --- | Insol. | | Emulsion in Aqueous |
| Quaternary C | 0.1 | 1.1 | --- | 3rd Phase | | --- | nil | nil | 0.8 | nil | nil | Good |
| Cetyldimethyl-benzylammonium chloride | 0.1 | 1.0 | --- | 63 | 2 | 1.0 | 46 | 1 | 0.9 | 50 | 1 | Good |
| Hyamine 10X | 0.1 | 1.1 | 1.2 | 88 | 8 | --- | Insol. | | --- | Insol. | | Fair |
| Hyamine 1622 | 0.1 | 1.1 | 1.2 | --- | --- | --- | Insol. | | --- | Insol. | | Fair |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

E. Miscellaneous Nitrogen Compounds

| Compound | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sym-Diphenyl-ethylenediamine | 0.1 | 1.0 | --- | Emulsion | | --- | Emulsion | | --- | Emulsion | | Emulsion |
| Benzidine | 0.1 | 1.0 | --- | nil | nil | 1.1 | nil | nil | 1.0 | nil | nil | Poor |
| Duomeen 12 | 0.1 | 0.9 | 1.2 | Ppt. | | 1.2 | 9 | < 1 | --- | --- | --- | Poor |
| Duomeen C | 0.1 | 0.9 | 1.2 | --- | --- | 1.2 | Ppt. | | 0.9 | nil | nil | Poor |
| Duomeen S | 0.1 | 0.9 | 1.2 | 46 | 1 | --- | Ppt. | | 0.9 | 8 | < .1 | Poor |
| N,N,N',N'-tetra-(2-ethylhexyl)-ethylenediamine | 0.1 | 1.0 | 1.1 | 10 | < 1 | --- | 4 | < .1 | 0.8 | 3 | < .1 | Good |
| N,N'-bis(α-methylbenzyl)-ethylenediamine | 0.2 | 1.0 | 1.5 | 18 | < 1 | 1.6 | 21 | < 1 | 0.9 | 13 | < 1 | Poor |
| Cetyldimethyl-amine oxide | 0.1 | 1.1 | 1.2 | --- | --- | --- | 22 | < 1 | --- | 9 | < 1 | Poor |
| 4-n-Amylpyridine | 0.1 | 1.0 | 1.1 | nil | nil | 1.1 | nil | nil | 0.9 | nil | nil | Good |
| 5-Ethyl-2-methyl-piperidine | 0.1 | 1.1 | 1.3 | nil | nil | 1.2 | nil | nil | 1.1 | nil | nil | Good |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

E. Miscellaneous Nitrogen Compounds (Cont'd.)

| Compound | Conc.** M | Init. Aq. pH | Chloroform Final pH | Chloroform Extn. % | Chloroform $E_a^o$ | Benzene Final pH | Benzene Extn. % | Benzene $E_a^o$ | Benzene (Prewashed)* Final pH | Benzene (Prewashed)* Extn. % | Benzene (Prewashed)* $E_a^o$ | Phase Separation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Heptadecyl-glyoxalidine | 0.1 | 1.0 | --- | 62 | 2 | --- | Insol. | | --- | Insol. | | Poor |
| 1-Hydroxyethyl-2-heptadecenyl-glyoxalidine | 0.1 | 1.0 | 1.1 | 54 | 1 | 1.1 | nil | nil | 0.9 | nil | nil | Poor |
| Decahydro-quinoline | 0.1 | 1.0 | 1.1 | 12 | < 1 | 1.1 | 11 | < 1 | 0.9 | nil | nil | Good |
| Laurylmorpholine | 0.1 | 1.0 | 1.0 | --- | --- | --- | nil | nil | 0.9 | *<1 | <.1 | ---- |
| Dimethyl-p-toluidine | 0.1 | 1.0 | 1.0 | 3 | <.1 | 1.0 | nil | nil | 0.9 | *nil | nil | Good |
| Amine C | 0.1 | 1.1 | --- | 3rd Phase | | --- | nil | nil | 0.9 | nil | nil | Good |
| Amine O | 0.1 | 1.1 | --- | --- | --- | 1.2 | nil | nil | --- | Emulsion | | ---- |
| Methyllauryl-nitrosoamine | 0.1 | 1.0 | --- | 4 | <.1 | --- | nil | <.1 | 0.9 | *nil | <.1 | Poor in Benzene |

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

Extraction Conditions:

Organic contacted with aqueous (1:1 ratio) containing ~1 g/l uranium and 1M $SO_4$ for 5 min. Phases then allowed to separate and analyzed for uranium.

*The solution of reagent in benzene was prewashed with a dilute sulfuric acid solution before the uranium extraction test. Where marked (*), the prewash solution used was ~0.1M $H_2SO_4$, where not so marked, ~0.5M $H_2SO_4$.

**Reagents were made up to the indicated molarity on basis of the theoretical molecular weight (for mixtures, the average molecular weight indicated by vendor), on the assumption of 100% assay for all except the following compounds, for which assays or acid equivalents were known:

| | | |
|---|---|---|
| Arquad S, | theo. mol. wt. 306, | assay 50% |
| Arquad 2HT, | 533 | 75% |
| Arquad 2C, | 360 | 75% |
| Roccal, | 318 | 50% |
| Cetyldimethylamine Oxide, | 285 | 20% |
| | | |
| Armeen 2C, acid equivalent, | 386 | |
| Armeen 2HT | 511 | |
| Primene 81T | 206 | |
| Primene JMT | 316 | |

cf. Appendix A for subsequent purity-level evaluations for the various reagents.

with benzene as the diluent. Semipermanent emulsions were formed with both solvents necessitating a centrifugal separation of the phases. After separation, in almost every case, a small amount of waxy solid was present at the interface. This solid contained small amounts of uranium and, presumably, most of the original amine.

2. Good uranium extractions were obtained with several branched-chain primary amines and most of these compounds showed no tendency toward emulsion formation. However, a number of these amines were distributed appreciably to the aqueous liquor. Only three of the compounds tested appeared acceptable from the standpoint of both extraction and solubility loss, i.e., Primene JMT, C&CCC 21F81, and C&CCC 21F79.

## Secondary Amines

1. Normal chain secondary amines with 10-12 carbons per chain, e.g., di-n-decylamine and dilaurylamine, gave excellent extraction of uranium with inappreciable loss of reagent to the aqueous solutions. With shorter chain compounds, the solubility losses were appreciable and, probably as a direct result, the uranium extractions were much lower. The longer chain compounds gave satisfactory performance from the standpoint of both extraction and loss but were limited in usefulness due to limited solubility in the organic diluent. Maximum concentrations obtainable with 14-16 carbons per chain were about 0.05M, and with 18 carbons per chain, about 0.01M. Phase separation difficulties were encountered in only two cases and these were with the soluble short chain compounds.

2. Several of the alicyclic and branched-chain amines have also given excellent uranium extractions without interference from emulsion formation. Unfortunately, with the compounds tested thus far, the better extractants also gave evidence of appreciable loss to the aqueous phase. Other compounds of higher molecular weight are being procured for further studies.

3. Tests have been made on three secondary amines in which one of the alkyl groups carries an aromatic substituent, viz., tetradecyl(3-phenylpropyl)amine, N-(2-ethylhexyl)-

α-methylbenzylamine, and N-(2-ethylhexyl)-α-xylyl-benzylamine. The first of these compounds gave excellent extractions of uranium and showed little, if any, loss through solubility. Good extractions were also obtained with the second compound but the apparent reagent loss was high. The third reagent was a poor extractant.

4. The two aromatic secondary amines tested thus far, n-butylaniline and p,p'-dioctyldiphenylamine, were not good reagents.

## Tertiary Amines

1. Most of the symmetrical and unsymmetrical aliphatic normal chain tertiary amines of high molecular weight proved to be excellent extractants for uranium, showing high extraction coefficients and inappreciable loss to the aqueous liquors, and giving no apparent troubles in separation of the phases. Limited performance was encountered with only two of these reagents which, in each case, contained one or more very long hydrocarbon chains, i.e., methyldi-n-octadecylamine and dimethyl-n-octadecylamine. The former showed limited solubility in the organic diluents, similar to the (secondary) di-n-octadecylamine, and semipermanent emulsions were formed in each test with the latter, similar to those experienced with (primary) n-octadecylamine.

2. The low molecular weight tertiary amines, like the secondaries, exhibited the ability to complex (and extract) uranium but these reagents were again unacceptable due to their high distribution to the acid sulfate liquor.

3. The aromatic tertiary amines tested thus far, diethylnaphthylamine, di-n-butylaniline, and ethylbenzylaniline, have not been good reagents. Insignificant extractions were also obtained with dimethylbenzyl- and tribenzylamine. It should be noted, however, that most of these compounds were of a low molecular weight and thus may have been appreciably lost to the aqueous phase.

4. Somewhat encouraging results were obtained with the commercially available β-hydroxyethyldilaurylamine. Extraction was poor, however, by the few other amines tested in this class, i.e., alkyl-bis(hydroxypolyethoxy)-amines such as Ethomeens S-15, S-60 and C-15.

## General

1. The importance of structural (steric) effects on the complexing ability of the amines is indicated by comparative extraction results with several of the tertiary and secondary compounds. With the tertiary amines, extractions were definitely impaired when two or more of the alkyl radicals were branched in close proximity to the nitrogen: Compare tri(2-ethylhexyl)- with tri-n-octylamine, di(2-ethylhexyl)lauryl- with dihexyllaurylamine, and methyldi(2-ethylhexyl)- with methyldi-n-octylamine. Other extraction differences which may be at least partially due to differences in structures are as follows: Di(2-ethylhexyl)amine > 2-ethylhexyl-2-pentylnonylamine, di(2-ethylhexyl)amine > C&CCC 16F27, tetradecyl(3-phenylpropyl)amine > N-(2-ethylhexyl)methylbenzylamine > N-(2-ethylhexyl)-$\alpha$-xylylbenzylamine.

2. Comparison of the results with chloroform and benzene in Table 1 shows that the nature of the solvent can have an important influence on the extraction process, the magnitude and direction of which is not necessarily the same with different amines. A qualitative explanation of the differences can be proposed, based on the assumption that association exists between the molecules of amine and the polar chloroform. Such an association would be expected to give rise to two opposing effects: First, it should decrease the loss of amine by distribution to the aqueous phase. Second, it should also interfere to some extent with the extraction process, by its competition for the amine. The net results should be an improvement of the extraction (otherwise very poor) obtainable with the low molecular weight amines which are almost completely lost to the aqueous phase from benzene, but an impairment of the extraction (otherwise very good) with the higher-weight amines which show little or no loss to the aqueous phase. It is unlikely, however, that a quantitative explanation could be developed on this simple basis; the interactions in the chloroform-amine system are probably quite complex. Some demonstration of this has been encountered during attempts to measure the loss of amine from these solutions (cf. Section D), where it was found that the sulfuric acid which had been extracted into these systems could not be removed by contact with a two-fold excess of 0.1N sodium hydroxide solution. Further studies of the effects of solvents are being included as a part of the fundamental program described above.

3. As mentioned previously, the amines will react with aqueous solutions of acids to form the corresponding amine salts. Thus, in cases where the solvents had not been pretreated with sulfuric acid, the extractions as shown in Table 1 were accompanied by an increase in the aqueous pH. The magnitude of this increase (0.1-0.2 units in Table 1) would vary in different extraction systems dependent upon the sulfate concentration, the amine concentration and the initial acidity. However, since the acidic sulfate liquors are well buffered and since the amine requirements for uranium extractions are small, the pH change under any process circumstances visualized should not be large. Changes obtained in process test work have ordinarily been as follows: pH of 1 $\longrightarrow$ 1.15, pH of 1.5 $\longrightarrow$ 1.7, pH of 1.8 $\longrightarrow$ 2.1.

4. Of the compounds examined thus far, the following have been considered worthy of further study: Primary Amines - Primene JMT, C&CCC 21F81 and possibly C&CCC 21F79; Secondary Amines - di-n-decyl-, dilauryl-, tetradecyl(3-phenylpropyl)-, and possibly C&CCC 16F27 and the Armeen 2C mixture; and Tertiary Amines - methyldi-n-decyl-, methyldilauryl-, propyldi-n-decyl-, tri-n-octyl-, tri-n-decyl-, trilauryl-, dihexyllauryl-, possibly dibutyllauryl- and, because it is commercially available, possibly β-hydroxyethyldilauryl-.

## Quaternary Ammonium Compounds

1. Eleven commercially available quaternary salts have been included in the preliminary test series; these results are presented in Section D of Table 1. Several of these reagents gave moderate extractions into chloroform ($E_a^o$ = 1 to 8) but only three of the reagents were even weakly effective in benzene ($E_a^o$ = 0.4 to 1). On the basis of these data, it appears that the quaternary compounds have a much lower order of extraction power than do the simple primary, secondary and tertiary amines.

   A firm conclusion as to the comparative merits of the two type of extractants, however, must await the completion of additional tests with a wider variety of "better" reagents. It may be noted that most of the compounds in Section D of Table 1 were insoluble in benzene. Also, as contrasted to the simple amines, most of the quaternary compounds tested were in the form of

halide salts; thus the introduction of halide ions into the system could adversely affect extractions with the latter reagents if the alkylammonium ions have a higher order of affinity for the halide than for the sulfate ions.* At present, several of the more promising commercial compounds are being converted to a more desirable form such as the sulfate or carbonate, and other new and perhaps more likely compounds are being prepared. These reagents will be used for further tests of uranium extraction from acidic sulfate solutions and will also be evaluated as possible uranium extractants from basic liquors.**

## Other Organonitrogen Compounds

The screening tests have been extended briefly beyond the simple amines and quaternary ammonium compounds to other types of organonitrogen reagents with, thus far, little success. It should be noted, however, that the particular reagents examined were those which happened to be at hand. They may not have been particularly good choices for solvent extraction purposes since they were of low molecular weight and thus may have been readily lost to the aqueous liquor. A much wider variety of compounds must be studied before making any generalization about the veritable host of such compounds that are available.

---

*With the strong base (quaternary ammonium) ion exchange resins, the affinity for chloride is greater than for sulfate.

**The primary, secondary, and tertiary amines are ineffective extractants from strongly basic solutions such as the sodium carbonate liquors, presumably because their ionization is suppressed. Reagents which are salts of strong bases, such as the quaternary ammonium compounds, might be expected to show uranium extraction comparable to the sorption with strong base anion exchange resins. Preliminary results with a few compounds have shown some extraction.

## B. CHOICE OF DILUENT

The diluent to be used in the extraction process must conform to a number of criteria which in a practical sense are as important as those for the extraction reagent itself. The primary characteristics required of the diluent for uranium extraction to be obtained are (1) immiscibility with the aqueous solution, (2) ability to dissolve the reagent and the extracted uranium complex, and (3) freedom from interfering interaction with the reagent. In addition, for practical application the diluent must also have a low vapor pressure and high flash point, low toxicity, low mutual solubility with the aqueous phase in contact, chemical stability in the system, suitable density and viscosity for ready separation from the aqueous phase, freedom from tendency toward emulsification, and must be available in a quantity and at a cost commensurate with the intended operation.

In determining the optimum combination of these characteristics that might be obtained in extractions with the amines, a number of "screening" type tests have been made in a manner somewhat similar to those described in Section A for the reagents. Extractions by means of secondary and tertiary amines (di-n-octylamine, di(2-ethylhexyl)amine, tri-n-octylamine, and methyldi-n-octylamine) in a variety of diluents were examined. From these tests, the diluent types which appeared most likely to meet the specifications listed were selected and further examined in regard to their compatibility with the extraction process over a range of extraction conditions. The more important observations and conclusions which can be drawn from the test results obtained thus far may be itemized as follows:

1. From preliminary survey tests, it was found that good extraction performance could be obtained with all of the amines tested when the diluent was benzene, toluene, xylene, or one of the group of highly aromatic petroleum products such as Amsco D-95, Amsco G, Solvesso 100, Solvesso 150, Petbyco Hi-Flash Naphtha and Petbyco Solvent F-80. With the aliphatic hydrocarbons (e.g., kerosene), on the other hand, only the long-chain symmetrical tertiary and some branched-chain secondary amines gave acceptable performance; the other amines tested were precipitated from these solvents as the corresponding amine salt or uranium-amine-sulfate complex when contacted with the acidic sulfate liquor. Certain of the chlorinated hydrocarbons such as carbon tetrachloride and trichloroethylene gave consistently

good performance, whereas the results obtained with various other solvents such as chloroform, nitrobenzene and methyl-isobutyl ketone were varied with different amines. These latter solvents as also benzene would not be of interest for process application due to their failure to meet several of the specifications described above.

2. The long-chain symmetrical tertiary amines, e.g., tri-n-decylamine, were found to be compatible with a wide range of hydrocarbon diluents, even including plain kerosene under favorable conditions. The straight-chain secondary amines, e.g., di-n-decylamine, were compatible with a much narrower range of diluents, and under some conditions were limited to the hydrocarbon diluents of highest aromatic content. The unsymmetrical tertiary amines and the branched secondary amines appeared to be intermediate in the degree of aromaticity required of the diluent.

3. The compatibility of diluent with amine was affected by the composition of the aqueous liquor, including particularly the presence or absence of uranium (see below), the sulfate concentration, and the pH. For a given amine and diluent, the probability of amine sulfate precipitation or third liquid phase formation was greater at high sulfate concentration and low pH, less at low sulfate concentration and higher pH up to at least pH 2.

4. The temperature was an important factor in amine-diluent compatibility for at least the straight-chain secondary amines, the solubility of the amine sulfate being greater at higher temperature (cf. Table 3).

These effects of diluent type, amine type, and extraction conditions on the amine-diluent compatibility are interdependent, as is illustrated in Table 2. This table shows uranium extraction results for several different amines in benzene, Amsco D-95, and kerosene, from sulfate solutions of varying sulfate concentration and pH, and from sulfate leach liquors. The extraction coefficients were usually somewhat lower in Amsco D-95 than in benzene and still lower in kerosene. The straight-chain secondary amines, di-n-decyl- and dilauryl-, and also the unsymmetrical tertiary methyldi-n-decylamine, showed precipitation or third liquid phase formation in every test made with kerosene as the diluent; in addition, emulsions were formed with di-n-decylamine in Amsco D-95 at pH 0.5, which may have been indication of separation of a liquid or a solid. The three branched-chain secondary amines tested were free of third phase formation in kerosene as well as in the aromatic diluents. The symmetrical tertiary amines illustrate an

Table 2

COMPARISON OF DILUENTS:

EFFECT OF SULFATE CONCENTRATION AND pH

| Amine (0.1M) | Aqueous Solution[a] Sulfate M | pH Initial | pH Final | U Extraction Coefficient, $E_a^o$ Benzene | Amsco D-95[b] | Kerosene |
|---|---|---|---|---|---|---|
| Di-n-decylamine | 0.5 | 0.4 | 0.5 | 20 | Emul. | 3rd Ph. |
| | | 1.1 | 1.2 | 120 | 70 | " |
| | | 1.8 | 2.1 | 500 | 220 | " |
| | 1.0 | 0.4 | 0.5 | 10 | Emul. | " |
| | | 1.0 | 1.1 | 40 | 20 | " |
| | | 1.9 | 2.2 | 230 | 75 | " |
| | Syn. Leach Liq. | | | 60 | 30 | " |
| Dilauryl | Leach Liq. | | | 40 | 20 | |
| | Syn. Leach Liq. | | | 35 | 35 | Ppt. |
| Di(2-ethylhexyl) | Leach Liq. | | | | | 7 |
| | Syn. Leach Liq. | | | 70 | 70 | |
| C&CCC 15F53[c] | Leach Liq. | | | | | 8 |
| | Syn. Leach Liq. | | | 40 | | |
| C&CCC 16F27[c] | Leach Liq. | | | 6 | | 6 |
| | Syn. Leach Liq. | | | | 9 | |
| Methyldi-n-octyl | Leach Liq. | | | 40 | 10 | |
| | Syn. Leach Liq. | | | 60 | 20 | |
| Methyldi-n-decyl | 1.0 | 1.0 | 1.1 | 90 | 20 | 3rd Ph. |
| | Leach Liq. | | | 50 | | (3rd Ph. in "Varsol) |
| | Syn. Leach Liq. | | | 100 | | |

Table 2 (Cont'd.)

COMPARISON OF DILUENTS:

EFFECT OF SULFATE CONCENTRATION AND pH

| Amine (0.1M) | Aqueous Solution[a] Sulfate M | pH Initial | pH Final | U Extraction Coefficient, $E_a^o$ Benzene | Amsco D-95[b] | Kerosene |
|---|---|---|---|---|---|---|
| Tri-n-hexyl | Leach Liq. | | | 130 | | |
| | Syn. Leach Liq. | | | 200 | 130 | 3rd Ph. |
| Tri-n-octyl | 0.5 | 0.4 | 0.5 | 40 | 40 | 3rd Ph. |
| | | 1.1 | 1.2 | 200 | 160 | 80 |
| | | 1.9 | 2.1 | 520 | 210 | 10 |
| | 1.0 | 0.2 | 0.2 | 20 | 8 | 3rd Ph. |
| | | 1.0 | 1.1 | 70 | 60 | 30 |
| | | 1.9 | 2.0 | 270 | 110 | 20 |
| | 1.5 | 0.05 | 0.2 | | 2 | 3rd Ph. |
| | | 1.0 | 1.1 | | 30 | 3rd Ph. |
| | | 2.1 | 2.2 | | 50 | 10 |
| | 2.0 | < 0 | < 0 | | 1 | 3rd Ph. |
| | | 1.0 | 1.0 | | 10 | 3rd Ph. |
| | | 2.0 | 2.1 | | 40 | 6 |
| | Syn. Leach Liq. | | | 160 | 130 | 80 |
| Tri-n-decyl | 0.5 | 0.4 | 0.4 | 30 | 20 | 25 |
| | | 1.0 | 1.1 | 110 | 60 | 80 |
| | | 1.8 | 2.0 | 350 | 100 | 60 |
| | 1.0 | 0.4 | 0.5 | 20 | 10 | 10 |
| | | 1.0 | 1.1 | 50 | 20 | 30 |
| | | 1.8 | 2.0 | 180 | 40 | 25 |
| | 1.5 | 0.05 | 0.05 | | | 2 |
| | | 1.0 | 1.1 | | | 30 |
| | | 2.1 | 2.2 | | | 30 |

Table 2 (Cont'd.)

COMPARISON OF DILUENTS:

EFFECT OF SULFATE CONCENTRATION AND pH

| Amine (0.1M) | Aqueous Solution[a] Sulfate M | pH Initial | pH Final | U Extraction Coefficient, $E_a^o$ Benzene | Amsco D-95[b] | Kerosene |
|---|---|---|---|---|---|---|
| Tri-n-decyl | 2.0 | < 0 | < 0 | | | 3rd Ph. |
| | | 1.0 | 1.1 | | | 10 |
| | | 2.0 | 2.0 | | | 20 |
| | Syn. Leach Liq. | | | 110 | 90 | |
| Trilauryl | Syn. Leach Liq. | | | 200 | 180 | |

a) Aqueous solutions used (phase ratio $2^a:1^o$):

1) Reagent solutions, 1 g U/liter, sulfate and pH as shown.

| | 2) Leach Liquor | 3) Syn. Leach Liquor |
|---|---|---|
| U | 1.25 g/liter | 1.25 g/liter |
| Fe | 0.10M | 0.10M |
| Al | 0.12M | 0.12M |
| Ca+Mg | 0.06M | 0 |
| Na+K | 0.03M | 0 |
| $SiO_2$ | 0.001M | 0 |
| F | 0.09M | 0.09M |
| $PO_4$ | 0.02M | 0.02M |
| $SO_4$ | 0.5M | 0.5M |
| pH | 0.83 | 0.8 |

b) Amsco D-95: High boiling, highly aromatic petroleum product, Kauri-Butanol value = 97.

c) C&CCC 15F53 and 16F27: Symmetrical secondary amines of branched alkyls, molecular weights 270 and 354.

increasing compatibility with kerosene as the size of the molecule increases: tri-n-hexylamine gave a third phase in contact with a leach liquor; tri-n-octylamine did not give a third phase with the leach liquor but did with all simple sulfate solutions at pH 0.5 or below, and at pH 1 when the sulfate concentration was 1.5M or higher; tri-n-decylamine gave a third phase only at the highest sulfate concentration and lowest pH tested, i.e., 2M sulfuric acid.

Since the solubility of the amine salt has proved to be an important factor in the choice of diluent, direct measurements of the solubility are being made. Some solubilities in Amsco D-95 are shown in Table 3. It may be noted that the sulfates of the straight-chain secondary amines showed a large temperature coefficient of solubility, while the solubilities of the tertiary amine sulfates were essentially constant from 2° to 50°C. These measurements will be extended to include other important amines and other diluents, and similar measurements will also be made with the amine bisulfates.

In addition to the data above, numerous other studies of the various diluents have been made but in a less systematic manner so that the results are less adaptable to a tabular presentation. The observations which have been made from these tests are as follows:

1. Reasonable extractions and phase separations were obtained using the branched primary amines, C&CCC 21F81 and Primene JMT, in kerosene. As would be expected, when the kerosene was modified with some aromatic diluent the performance of these amines as well as the branched secondaries and symmetrical tertiaries was better, and appeared to be intermediate between that obtained with the kerosene and that with aromatic products alone.

2. With several amine-diluent mixtures, the tendency toward third phase formation, presumably of the amine sulfate or bisulfate salt, was more pronounced if the liquors contacted were "pure" acidic sulfate solutions, containing neither uranium nor other metallic ions. Di-n-decylamine, 0.1M in Amsco D-95, for example, gave immediate third phase formation at 25°C when contacted with a "pure," 1M sulfate, pH = 1, liquor. Similar results were obtained with the longer chain dilaurylamine in Amsco G (Kauri-Butanol value - 87)* and also with tri-n-octylamine in kerosene, whereas

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*The Kauri-Butanol value (cf. ASTM Method D1133-50T, 1952) is a measure of "solvent power," and is higher for aromatic than for aliphatic solvents. The K.-B. value of toluene is 105.

Table 3

SOLUBILITY OF AMINE SULFATE IN AMSCO D-95

| Amine (as normal amine sulfate[a]) | Solubility,[b] (molarity of amine): 2° | 5° | 20° | 25° | 50°C |
|---|---|---|---|---|---|
| Di-n-decyl | | 0.06 | 0.12 | 0.22 | ⩾1.44 |
| Dilauryl, Batch F | 0.02[c] | | 0.10 | 0.20 | ⩾1.64 |
| Methyldi-n-octyl, Batch A | 2.2 | | 2.2 | 2.4 | ⩾2.4 |
| Dibutyllauryl, Batch A | 2.0 | | 1.8 | 2.4 | ⩾2.4 |
| Tri-n-octyl, Batch F | 1.5 | | 1.5 | 1.7 | |

a) Amine salt prepared by precipitation from methanol solution by addition of 10% excess sulfuric acid (based on $Am_2SO_4$), and dried with gentle heating under vacuum.

b) Solubility determined by addition of successive increments of diluent until complete dissolution was obtained, except as noted.

Temperature range estimated to be ± 1°C.

c) Solubility determined by titration of saturated organic phase.

the same effects were not noted with these amines or with C&CCC 21F81 (branched primary), ditridecyl- (branched secondary), and tri-n-decyl- (symmetrical tertiary) when the solvent was Amsco D-95 (Kauri-Butanol value - 97). In cases where a third phase tended to form, the tendency was observed to increase with decreasing pH and increasing sulfate concentration, suggesting that the bisulfate salt was less soluble in the organic diluent than the sulfate salt. On the other hand, if the system contained appreciable uranium, or if it was held at a sufficiently high temperature or if the solvent was modified with several percent of a long chain alcohol, a third phase could be avoided in all the cases mentioned. The presence of iron in the organic phase also appeared to retard the formation.

3. Since the liquor in the lower stages of a countercurrent extraction process is barren of uranium (although not of iron), it seems probable from the above observations that some of the amine-diluent mixtures might give operational difficulties in process application which would not be noticed in single stage experimental shakeouts where the uranium is present. In actual countercurrent tests with, for example, di-n-decylamine in Amsco D-95, these difficulties were not encountered. It is likely, however, that the conditions were very close to borderline for successful operational practice.

In general, from the results thus far, it may be observed that the diluents of widest application in the amine extraction process are those of highest aromaticity. The amines of widest application are the symmetrical tertiary amines, which can be used with a wide range of diluent types, while the branched-chain secondary amines and the unsymmetrical tertiary methyldialkylamines are somewhat more stringent in their demands on the diluent, and the straight-chain secondary amines apparently require a diluent of the highest aromaticity (or one modified with, e.g., a long-chain alcohol) in order to be operable. The degree of compatibility between amine and diluent is also found to vary with the extraction conditions. Thus, the combination of a better amine with a better diluent (e.g., tri-n-octylamine and Amsco D-95) gives a highly versatile solvent which can be used over a very wide range of extraction conditions. Combinations of the symmetrical tertiary amines or branched secondary amines with solvents or solvent mixtures of lower aromaticity are somewhat less versatile but should also be applicable over the range of conditions likely to be encountered with sulfate leach liquors. If a less versatile diluent such as kerosene is used with these

amines, or if a less versatile amine such as a straight-chain secondary is used with even the more versatile diluents, application can still be made under favorable extraction conditions, but if the conditions vary considerably the operation may require careful control.

Most of the tests described in subsequent sections of this report have been made with Amsco D-95 since, of the mineral spirits so far examined, this diluent has shown the widest compatibility with the various types of amines. Other tests are currently being made both on a laboratory and larger scale to further evaluate the optimum amine-diluent combinations for process application.

## C. SELECTIVITY FOR URANIUM

In the previous sections, it has been demonstrated that many amines are effective extractants for uranium from "pure" acidic sulfate solutions. Some of these, however, may be unacceptable extractants for solutions contaminated with other metal ions, either because the purity of the resulting uranium product is too low, or because the uranium extraction is inhibited by the competitive extraction of the contaminants. The ability of a reagent to extract uranium without excessive extraction of contaminants, i.e., its selectivity for uranium, is particularly important in the treatment of ore leach liquors, which ordinarily contain many other metal ions, e.g., iron, aluminum, sodium, magnesium, calcium, copper, nickel, vanadium, etc. The distribution and quantities of these ions vary widely, being dependent on both the composition of the ore and the type of leaching treatment used, but many of them are usually as high or even much higher in molar concentration than the uranium.

In tests to be described, the selectivity properties of a primary amine and several secondary and tertiary amines have been examined by contacting these compounds (0.1M, in hydrocarbon diluent) with acidic sulfate liquors containing those metals most commonly encountered in ore leach liquors. In some cases the tests were also extended to metals not usually found in uranium ores to determine, as a secondary objective, whether the amines might be useful in recovery processes other than for uranium. All

experiments were made by batch shakeouts in a separatory funnel, the extractions being measured in the usual way after the elapse of sufficient time for equilibration.

The aqueous liquors were prepared by dissolving the metal sulfate or oxide in a sulfuric acid solution and adjusting to the desired pH and sulfate level by the addition of water, sodium hydroxide, and/or sodium sulfate. Appropriate quantities of other salts were also added in cases where the effect of anions other than sulfate was being measured. In all initial tests, the concentrations of the metal ions ranged between 1 to 2 grams per liter. The extractions were repeated at a lower concentration in those cases where it appeared that the extraction coefficients had been limited by near saturation of the organic phase with the metal ion.

Results from the extraction of the pure acidic metal sulfate solutions with the amines are listed in Table 4. Tables 5 and 6 show how the presence of other anions in the sulfate liquor can affect the extraction of certain of these metals. In examining these data it should be remembered that the amines tested were not completely pure compounds, and the impurities may have given measurable extraction in some cases where the major constituent itself might have extracted little or even none of the metal ion. This effect can hardly be important in comparing large extraction coefficients, or large differences in the coefficients, but it may have been significant when only small quantities of the metal ion were involved. Thus, it seems safe to assume that, when the extractions were low, the coefficients to be expected of the absolutely pure compound would not be greater and might be less than the coefficients shown.

With these points in mind, some of the more important observations that may be made from examination of the selectivity data are as follows:

1. With few exceptions, the extraction coefficients for the metals increased with increasing pH, and with many of the metals this effect was very strong. The excepted cases were usually in tests where the quantity of metal in one of the two phases was so low that the coefficient measurements were sensitive to analytical error.

2. Of the three amine types examined, the primary amine showed by far the poorest selectivity; the selectivity of the secondary amines was good and the selectivity of the

## Table 4

## EXTRACTION OF VARIOUS METALS BY AMINES

| Head Aq. Soln. | | | Extraction Coefficients, $E_a^o$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | (Primary) | (Secondary) | | (Tertiary) | |
| Metal Ions g/l | $SO_4$, M | pH | C&CCC 21F81 | C&CCC 15F53 | Dilauryl-amine | Methyldi-n-octylamine | Tri-n-decylamine |
| **Iron(II)** | | | | | | | |
| 2.1 | 1.0 | 0.5 | | 0.002 | 0.004 | 3rd Ph. | 0.002 |
| 2.2 | " | 1.0 | | .002 | .01 | .004 | .002 |
| 2.1 | " | 1.8 | | .04 | .07 | .015 | .02 |
| 0.23 | " | 0.7 | *0.15 | | | | |
| 0.23 | " | 1.2 | * .08 | | | | |
| 0.23 | 0.26 | 0.7 | * .15 | | | | |
| 0.23 | " | 1.2 | * .2 | | | | |
| **Iron(III)** | | | | | | | |
| 1.9 | 1.0 | 0.5 | | .004 | .01 | 3rd Ph. | .003 |
| 2.0 | " | 1.0 | | .01 | .1 | .02 | .002 |
| 1.9 | " | 1.8 | | .2 | 1.3 | .1 | .05 |
| 0.23 | " | 0.7 | *30 | | | | |
| 0.23 | " | 1.1 | *25 | | | | |
| 0.23 | 0.26 | 0.6 | *20 | | | | |
| 0.23 | " | 1.2 | *250 | | | | |
| **Aluminum** | | | | | | | |
| 2.0 | 1.0 | 0.5 | .004 | < .001 | .02 | 3rd Ph. | .001 |
| 2.0 | " | 1.0 | .04 | .001 | < .001 | < .001 | .002 |
| 2.4 | " | 1.8 | .1 | .002 | .001 | .01 | .003 |
| 0.08 | " | 1.8 | .5 | | | | |

Table 4 (Cont'd.)

EXTRACTION OF VARIOUS METALS BY AMINES

| Head Aq. Soln. | | | Extraction Coefficients, $E_a^o$ (Primary) | (Secondary) | | (Tertiary) | |
|---|---|---|---|---|---|---|---|
| Metal Ions g/l | $SO_4$, M | pH | C&CCC 21F81 | C&CCC 15F53 | Dilauryl-amine | Methyldi-n-octylamine | Tri-n-decylamine |
| **Magnesium** | | | | | | | |
| 2.0 | 1.0 | 0.5 | < 0.001 | < 0.001 | 0.03 | 3rd Ph. | 0.001 |
| 1.9 | " | 1.0 | .006 | < .001 | .002 | .005 | < .001 |
| 2.0 | " | 1.8 | .02 | .001 | .001 | .005 | < .001 |
| **Calcium** | | | | | | | |
| 0.6 | 1.0 | 0.5 | .01 | .001 | .002 | 3rd Ph. | .001 |
| 0.6 | " | 1.0 | .03 | .01 | .004 | .015 | .015 |
| 0.8 | " | 1.8 | .9 | < .001 | .004 | .002 | .002 |
| 0.3 | " | 1.8 | .7 | | | | |
| **Zinc** | | | | | | | |
| 2.1 | 1.0 | 0.5 | .002 | < .001 | < .001 | 3rd Ph. | .001 |
| 2.1 | " | 1.0 | .004 | < .001 | .002 | .003 | < .001 |
| 2.7 | " | 1.8 | .02 | < .001 | .001 | .005 | .001 |
| **Manganese(II)** | | | | | | | |
| 2.1 | 1.0 | 0.4 | .003 | < .001 | < .001 | 3rd Ph. | < .001 |
| 2.1 | " | 1.0 | .015 | < .001 | < .001 | .002 | < .001 |
| 1.9 | " | 1.8 | .15 | < .001 | < .001 | .004 | < .001 |
| 0.25 | " | 1.8 | .09 | | | | |

Table 4 (Cont'd.)

EXTRACTION OF VARIOUS METALS BY AMINES

| Head Aq. Soln. | | | Extraction Coefficients, $E_a^o$ (Primary) | (Secondary) | | (Tertiary) | |
|---|---|---|---|---|---|---|---|
| Metal Ions g/l | $SO_4$, M | pH | C&CCC 21F81 | C&CCC 15F53 | Dilauryl-amine | Methyldi-n-octylamine | Tri-n-decylamine |
| **Chromium(III)** | | | | | | | |
| 1.7 | 1.0 | 0.4 | 0.15 | < 0.001 | < 0.001 | 3rd Ph. | < 0.001 |
| 1.8 | " | 1.0 | .04 | .001 | < .001 | .009 | < .001 |
| 1.7 | " | 1.8 | .15 | .01 | < .001 | .015 | .002 |
| 0.2 | " | 0.3 | .07 | | | | |
| 0.2 | " | 0.9 | .4 | | | | |
| 0.2 | " | 1.8 | 1.5 | | | | |
| **Molybdenum(VI)** | | | | | | | |
| 1.6 | 1.0 | 0.5 | 35 | 110 | 65 | 3rd Ph. | 150 |
| 1.9 | " | 1.0 | 140 | 370 | 200 | 370 | 120 |
| 2.0 | " | 1.8 | 2000 | 1600 | 3600 | 2000 | 3500 |
| 0.35 | 0.3 | 1.8 | 350 | | | | |
| **Nickel(II)** | | | | | | | |
| 2.3 | 1.0 | 0.4 | .002 | < .001 | 3rd Ph. | 3rd Ph. | < .001 |
| 2.3 | " | 1.0 | .004 | < .001 | < .001 | .002 | < .001 |
| 2.3 | " | 1.7 | .015 | < .001 | .002 | .004 | < .001 |
| **Copper(II)** | | | | | | | |
| 2.0 | 1.0 | 0.4 | .003 | .002 | 3rd Ph. | 3rd Ph. | .001 |
| 2.0 | " | 1.0 | .01 | < .001 | .001 | .003 | < .001 |
| 2.0 | " | 1.7 | .03 | < .001 | .002 | .007 | .001 |

Table 4 (Cont'd.)

EXTRACTION OF VARIOUS METALS BY AMINES

| Head Aq. Soln. | | | Extraction Coefficients, $E_a^g$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | (Primary) | (Secondary) | | (Tertiary) | |
| Metal Ions g/l | $SO_4$, M | pH | C&CCC 21F81 | C&CCC 15F53 | Dilauryl-amine | Methyldi-n-octylamine | Tri-n-decylamine |
| **Cobalt(II)** | | | | | | | |
| 2.2 | 1.0 | 0.4 | 0.002 | < 0.001 | 3rd Ph. | 3rd Ph. | < 0.001 |
| 2.2 | " | 1.0 | .006 | < .001 | < .001 | .003 | < .001 |
| 2.1 | " | 1.7 | .02 | < .001 | < .001 | .006 | < .001 |
| **Beryllium** | | | | | | | |
| 0.05 | 1.0 | 0.3 | .2 | | | | |
| .05 | " | 1.0 | .2 | | | | |
| .05 | " | 1.8 | 1.3 | | | | |
| **Cerium(IV)** | | | | | | | |
| 0.6 | 1.0 | 0.3 | > 50 | < .02 | < .02 | 3rd Ph. | 12 |
| 0.5 | " | 0.9 | > 50 | < .02 | .02 | .5 | 30 |
| 0.5 | " | 1.8 | > 50 | .02 | .1 | .8 | 80 |
| **Thorium** | | | | | | | |
| 1.8 | 1.0 | 0.4 | | .02 | | 3rd Ph. | .01 |
| 1.9 | " | 1.0 | | .2 | | .1 | .02 |
| 1.8 | " | 1.8 | | 2.5 | | .2 | .2 |
| 0.8 | " | 0.3 | >300 | .02 | 3 | | |
| 0.8 | " | 0.9 | >300 | .1 | >300 | | |
| 0.8 | " | 1.7 | >300 | 5 | >300 | | |
| **Zirconium** | | | | | | | |
| 0.25 | 1.0 | 0.9 | 400 | 15 | 35 | 15 | |

Table 4 (Cont'd.)

EXTRACTION OF VARIOUS METALS BY AMINES

| Head Aq. Soln. | | | Extraction Coefficients, $E_a^o$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | (Primary) | (Secondary) | | (Tertiary) | |
| Metal Ions g/l | $SO_4$, M | pH | C&CCC 21F81 | C&CCC 15F53 | Dilauryl-amine | Methyldi-n-octylamine | Tri-n-decylamine |
| **Uranium(IV)** | | | | | | | |
| 1.0 | 1.0 | 0.4 | 1100 | 1 | 20 | 3rd Ph. | 2 |
| 1.0 | " | 1.0 | 3000 | 6 | 180 | .7 | 5 |
| 1.0 | " | 1.7 | 1300 | | 120 | | 12 |
| | | | | | | | (Tri-n-octylamine) |
| **Vanadium(IV)**** | | | | | | | |
| 1.0 | 0.5 | 1.5 | | | < .1 | | < .1 |
| 1.0 | " | 1.8 | | | < .1 | | < .1 |
| 1.0 | " | 2.0 | | | < .1 | | < .1 |
| | | | | | (Di-n-decylamine) | | |
| **Vanadium(V)** | | | | | | | |
| 0.9 | 1.0 | 1.0 | | | 0.6 | 0.3 | |
| 0.9 | " | 1.5 | | | 2 | 1.5 | |
| 0.9 | " | 2.0 | | | 30 | 25 | |
| 0.9 | 0.5 | 1.0 | | | 1.5 | .3 | |
| 0.9 | " | 1.5 | | | 5 | 4 | |
| 0.9 | " | 2.0 | | | 80 | 20 | |

**Extraction Conditions:**

0.1M Amine in Amsco D-95, phase ratio 2 aqueous: 1 organic, except as noted.

*0.1M Amine in benzene, phase ratio 1:1.

**Acidic vanadium(V) sulfate solution reduced with Zn/Hg from +0.6 to -0.3 v, Pt vs. Sat. Calomel, giving a blue solution probably containing chiefly vanadyl sulfate.

tertiary amines, especially the symmetrical tertiary amines, was excellent. The particular branched secondary amine (C&CCC 15F53) tested exhibited better selectivity properties than the straight-chain (dilauryl) secondary amine.

3. Ferric iron was extracted strongly by the primary amine, weakly by the secondary amines and very little by the symmetrical tertiary amines. Extraction coefficients for ferric iron with the primary amine were higher than those for uranium. Ferrous iron, on the other hand, was not appreciably extracted by any of the amines tested.

4. Aluminum, calcium, chromium(III), and beryllium were extracted weakly by the primary amine but to an insignificant extent by the secondary and tertiary amines. Sodium, magnesium, zinc, copper(II), cobalt(II), nickel(II), and manganese(II) were not appreciably extracted by any of the amines.

5. Coefficients for extraction of thorium were very high for the primary and straight-chain secondary amines but quite low for the tertiary and branched secondary amine. Extractions of uranium(IV) were also very strong with the primary and straight-chain secondary amines and much weaker with tertiary and branched secondary amines. Zirconium extractions were high with all of the amines tested.

6. Vanadium(V) extractions were very low at pH of 1 or less ($E_a^o < 1$) but increased as the pH was raised. Extraction coefficients of $\sim$30 were obtained with all of the amines tested at a pH of $\sim$2. Vanadium(IV) was not appreciably extracted by secondary and tertiary amines regardless of the aqueous pH. Extraction of vanadium(IV) with primary amines was not tested.

7. The primary amine extracted cerium(IV) quite readily, whereas the results with the secondary and tertiary amines were contradictory. These tests are being repeated.

8. Molybdenum(VI) was extracted very strongly by all three classes of amines. Extraction coefficients for molybdenum were higher than for any other element tested.

9. Extractions of some of the metal ions were strongly affected by the presence of small concentrations of other anions such as fluoride or phosphate. Molybdenum extractions, for example, (Table 5) were drastically reduced by addition of small amounts of fluoride to the sulfate liquor (similar effects would be expected with ferric iron). When

small concentrations of phosphate were present, the molybdenum extractions remained essentially unaffected but the extractions of ferric iron were appreciably decreased. Conversely, the amount of phosphate extracted into the organic phase was decreased if either iron or aluminum were present in the aqueous solution (Table 6).

In addition to the tests tabulated, the extraction and stripping of cobalticyanide were examined briefly, since this ion has been reported to poison the strong-base anion exchange resins used to recover uranium from the sulfate leach liquors of the Rand gold ore cyanidization residues.[4] Cobalticyanide was strongly extracted, $E_a^o > 50$, by tri-n-octylamine (0.1M, in benzene) at pH 0.7. However, the extracted cobalticyanide was effectively stripped by 0.1M sodium hydroxide solution in a multicycle test; hence, there appears to be no poisoning of the reagent by this ion. (Similarly, the sorbed cobalticyanide can be eluted by basic solution from the weak-base anion exchange resins, in contrast to its retention by the strong-base resins.[5])

It is generally apparent from the foregoing observations that the tertiary, especially the symmetrical tertiary, amines show a remarkable preference for uranium over the other elements commonly found in uranium ores and should, in this regard, be applicable to sulfuric acid leach liquors from almost all of the current uranium sources. The secondary amines, although apparently somewhat less selective than the tertiaries, should also be adequate for process application. The primary amines have shown very poor selectivity, particularly in regard to ferric iron, and on this basis have been eliminated from any intensive consideration in subsequent "screening" tests. They do not, however, extract ferrous iron and, thus, might find application if the iron in the liquors were reduced. Attention will be given later to this possibility.

Of the elements expected to be associated with uranium, molybdenum, which appears in some ores, is the only one of those tested which offered any major selectivity problem with the secondary and tertiary amines. If the ores also contained fluoride, the molybdenum problem would apparently tend to diminish. In cases where the compositions are not so fortuitous and appreciable molybdenum is extracted, it is probable that the separation of uranium and molybdenum can be accomplished either in the stripping cycle or in a subsequent operation. Acid nitrate or chloride solutions (pH = 1), for example, will strip uranium from the organic solvent (see Section H) but will not remove molybdenum.

Table 5

EFFECT OF FLUORIDE AND PHOSPHATE ON MOLYBDENUM EXTRACTION

| Concn. In Head Soln., M: F | $PO_4$ | Final pH | Molybdenum Extraction Coeff., $E_a^o$ |
|---|---|---|---|
| 0 | 0 | 1.1 | >100 |
| 0 | 0.02 | 1.1 | >100 |
| 0 | 0.05 | 1.0 | >100 |
| 0.02 | 0 | 1.1 | 75 |
| 0.05 | 0 | 1.2 | 20 |
| 0.1 | 0 | 1.4 | 20 |
| 0.2 | 0 | 1.6 | 8 |

Extraction Conditions:

0.1M Di-n-decylamine in Amsco D-95.

Head solution, 0.5M $SO_4$, 0.9 g Mo/l, plus indicated F (as NaF) and $PO_4$ (as $H_3PO_4$); initial pH 1.0.

Phase ratio, 2 aqueous: 1 organic.

Subsequent removal of molybdenum can be accomplished by scrubbing the solvent with dilute sodium hydroxide. A single-step separation might also be possible by direct treatment of the organic phase with a solution of sodium hydroxide. Under these conditions, the uranium would be removed as a precipitate (see Section H), whereas most of the molybdenum would be expected to remain in the aqueous supernatant.

It is further apparent from the data in Table 4 that the amines might be useful in extracting other elements from sulfate liquors* such as thorium, zirconium and,, under certain conditions, vanadium. Because of the importance of vanadium as a co-product with uranium from carnotite type ores, attention has been centered first on this element. Additional tests are described in Section I, and process development studies will be described in subsequent reports. Process application to thorium has not yet been evaluated.

## D. DISTRIBUTION OF AMINE TO THE AQUEOUS PHASE

In addition to the essential properties of extraction power and selectivity, a useful extraction agent must be retained at effective concentration in the solvent phase without requiring excessive makeup. One of the important ways in which reagent may be lost is by distribution to the aqueous phase. In contrast to entrainment losses, this loss by aqueous solubility involves an equilibrium process, and hence can be evaluated in terms of the solvent and aqueous compositions. All of the amines which have shown good uranium extraction in the screening tests can be considered as insoluble in water, but the solubility of their salts may be significant in acidic solutions. Moreover, "insoluble" so used is a relative term. Some finite quantity of even the least soluble compounds will distribute to an aqueous phase, and solubilities even lower

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*The amines may also be of practical use in the extractions of several elements from liquors other than sulfate. In continued analogy with anion resins, the amines will perform quite differently with liquors wherein the principal anion is different.[3]

Table 6

EFFECT OF PHOSPHATE ON IRON(III)

AND ALUMINUM EXTRACTIONS

| Concn. in Head Soln., M | | | Uranium Extraction Coeff., $E_o^a$ | Final Concn. in Organic, g/l | | |
|---|---|---|---|---|---|---|
| $PO_4$ | Fe(III) | Al | | $PO_4$ | Fe(III) | Al |
| 0 | 0 | 0 | 60 | | | |
| 0 | 0.075 | 0 | 25 | | 0.44 | |
| 0 | 0 | 0.075 | 60 | | | 0.005 |
| 0.02 | 0 | 0 | 55 | 0.17 | | |
| 0.02 | 0.075 | 0 | 35 | 0.03 | 0.22 | |
| 0.02 | 0 | 0.075 | 55 | 0.08 | | 0.008 |
| 0.04 | 0 | 0 | 55 | 0.23 | | |
| 0.04 | 0.075 | 0 | 30 | 0.05 | 0.32 | |
| 0.04 | 0 | 0.075 | 45 | 0.15 | | 0.005 |
| 0.1 | 0 | 0 | 15 | 0.28 | | |
| 0.1 | 0.075 | 0 | 20 | 0.09 | 0.05 | |
| 0.1 | 0 | 0.075 | 20 | 0.21 | | 0.003 |

Extraction Conditions:

0.1M Di-n-decylamine in Amsco D-95.

Head solution, 0.5M $SO_4$, 1.0 g U/l, plus indicated Fe, Al (as sulfates), and $PO_4$ (as $H_3PO_4$); initial pH 1.0, final pH 1.0-1.1.

Phase ratio, 2 aqueous : 1 organic.

than 100 parts per million in the raffinate can represent excessive reagent loss in extractions from liquors in which the uranium concentration is very low.

Some information on the relative loss of different amines by distribution to the aqueous phase was apparent in the screening extraction tests, particularly in the effect of prewashing the organic phase with a dilute sulfuric acid solution (Section A). There, for example, in a series of symmetrical tertiary amines, tri-n-butylamine gave very little uranium extraction into benzene solution, tri-n-hexylamine gave good extraction at a concentration of 0.1M while at 0.01M extraction was impaired by prewashing, and tri-n-octylamine gave as high extraction with the prewash as without it. Similarly, in a series of symmetrical secondary amines, extraction was considerably impaired by prewashing when the extractant was di-n-heptylamine at 0.1M, or di-n-octyl- or di(2-ethylhexyl)amine at 0.01M, but extraction by di-n-decylamine was not affected.

In subsequent tests, a quantitative estimate of the amount of amine lost to the aqueous phase was obtained by means of multicycle extraction tests. Here, the uranium extraction obtained in each successive cycle was plotted against the cumulative volume of aqueous solution contacted. The slope of this loss curve gave the rate of amine loss into the aqueous phase. The results for several amines, which are generally consistent with the more precise measurements described below, were as follows:

| Amines in Benzene | Aqueous Solubility In Reagent Solution, 0.05M $SO_4$, pH 1 |
|---|---|
| Armeen 2C | 10 ppm |
| Methyldi-n-decylamine | 10 |
| C&CCC 21F81 | 30 |
| Primene JMT | 100 |
| Methyldi-n-octylamine | 200 |
| Tri-n-hexylamine | 400 |
| C&CCC 16F27 | 500 |

| Amines in Amsco D-95 | In Synthetic Leach Liquor 0.5M $SO_4$, pH 0.7 |
|---|---|
| Armeen 2-12 | 0 ppm |
| Armeen 2C | 0 |
| Tri-n-hexylamine | 700 |
| C&CCC 15F53 | 1500 |
| Di(2-ethylhexyl)amine | 1600 |

More precise and accurate measurement of the reagent loss was made by a method which was basically equivalent to the multicycle extraction tests, but which used a direct analysis for the amine concentration and also avoided the cumulative uncertainties of actual recycling. The amine concentration in the organic phase was determined by potentiometric titration with perchloric acid in nonaqueous medium,[6] the endpoint being detected by means of a Beckman Model G pH meter with glass and saturated calomel electrodes. Samples containing 0.02 and 0.2 milliequivalents could be titrated to within about ± 0.002 meq.

Each solubility loss measurement consisted of a series of batch equilibrations made simultaneously. A typical series used 5 ml samples of the organic phase with volumes of the aqueous phase (presaturated with the diluent used in the organic phase) giving aqueous:organic phase ratios over the range from 5 to 100. The phases were mixed in closed containers at room temperature, then allowed to separate. A portion of the clear organic phase was treated with a two-fold excess of 0.1N sodium hydroxide solution to strip out the extracted anions and to regenerate the free amine.* (Uranium was absent in these tests, to avoid the complication of precipitation in the basic strip.) The organic solution was then rinsed with an equal volume of water to remove any entrained base, and aliquots were titrated. Tests with methyldioctylamine showed that no measurable amount of amine was lost to the basic strip or to the water rinse.

*When the diluent used was chloroform, the treatment as described with sodium hydroxide solution failed to strip out the extracted sulfate. Hence, when tests were made with chloroform solutions, the chloroform was removed from the organic phase samples by repeated evaporation with benzene before the sodium hydroxide treatment.

The loss curve obtained by plotting each final amine concentration against the corresponding phase ratio represented the curve which would be obtained from an ideal recycle process, giving directly the amount of amine retained at any stage. If the loss of amine conformed to a distribution coefficient essentially constant over the resulting range of concentrations, a logarithmic loss curve should be found. If, on the other hand, the transfer of amine were limited by saturation of the aqueous phase, the loss curve should be a straight line over the entire range in which saturation was maintained. Some examples of the curves actually obtained are shown in Figure 1, ranging from no measurable loss to a very high rate of loss. Many of the curves, like curve IV in the figure, showed linear loss, while none conformed well to a logarithmic loss curve.

Evidence has been found in several types of tests (see Appendix C) that the amine sulfates may exist in hydrocarbon diluents in some form (e.g., a colloidal dispersion) in which the amine activity is constant over a wide range of nominal concentrations. If this is true of the amines which were used in the solubility loss measurements, then a constant distribution coefficient ($a_a/a_o$) leads directly to a constant activity of amine in the aqueous phase, and a linear loss curve.

Curves like II and III in Figure 1 were given by several amines, showing a rapid drop at low aqueous:organic ratios followed by a much slower rate of loss at higher ratios. The best explanation that can be offered at present for such behavior is that the principle amine contained a significant admixture of other titratable bases which were more water-soluble, perhaps because of low molecular weight. Curves like V, in which a small but analytically significant titer persisted after rapid loss of most of the amine, suggested that here a small amount of a less water-soluble base was also present.

The solubility loss rates measured for nineteen amines in a variety of systems are summarized in Table 7. The form in which these data are presented is based on the assumptions discussed above, namely, (1) that some of the amine samples contained a relatively soluble fraction that was more readily lost than the principal amine, and (2) that the characteristic loss curve for an absolutely pure amine should be a straight line. Accordingly, the last two columns present the fraction readily lost expressed as per cent of the initial quantity of amine, and the subsequent steady-state loss rate expressed as parts of amine per

Figure 1

LOSS OF AMINE TO AQUEOUS PHASE

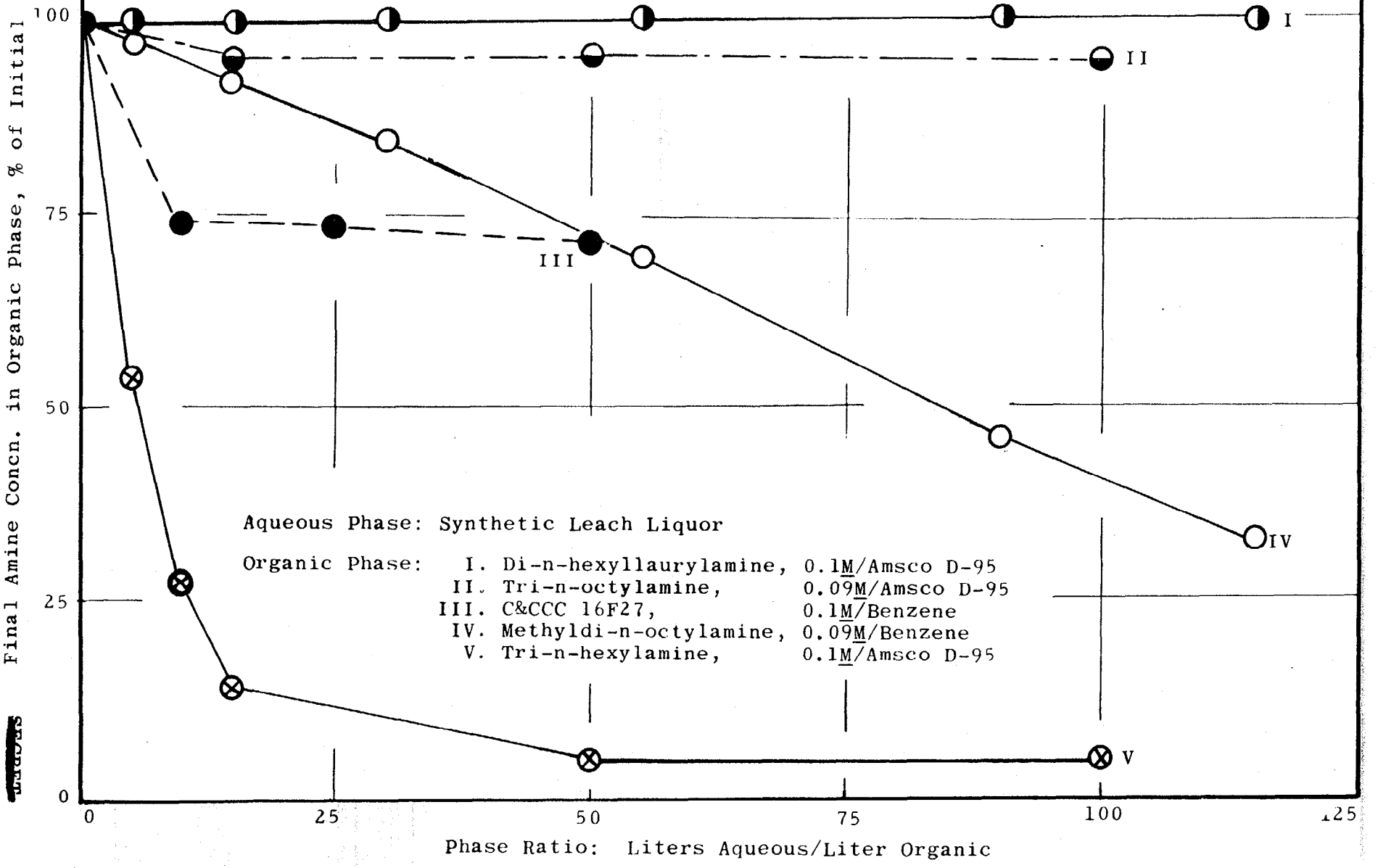

Table 7

LOSS OF AMINE TO AQUEOUS PHASE

| Organic Phase | | | | | Aqueous Phase[a] | | | Loss of Amine | |
|---|---|---|---|---|---|---|---|---|---|
| Amine | Batch | Mol. Wt. | Init. Concn. M | Diluent | Solute | Concn. M | pH | Fraction Readily Lost, % of Init. | Steady-State Loss ppm/aq |
| **Primary** | | | | | | | | | |
| Armeen 14D | A | 213 | 0.095 | Benzene | | Water | | 1 | 0 |
| | | | 0.193 | Benzene | Syn. Leach Liquor[e] | | | | $>4x10^{4g}$ |
| | | | .191 | D-95 | " | " | " | | $>4x10^{4g}$ |
| C&CCC 21F81 | A | 255 | 0.099 | Benzene | Syn. Leach Liquor | | | 0 | 0 |
| | | | .010 | " | " | " | " | 0 | < 5 |
| | | | .096 | D-95 | " | " | " | 0 | 15 |
| | | | .099 | Kerosene | " | " | " | 0 | 20 |
| **Secondary** | | | | | | | | | |
| Di-n-heptyl | A | 213 | 0.102 | Benzene | Syn. Leach Liquor | | | 25 | 590 |
| | | | .099 | D-95 | " | " | " | 30 | 770 |
| | | | .100 | $CHCl_3$ | " | " | " | 20 | 90 |
| Armeen 2-8 | A | 241 | 0.104 | Benzene | Syn. Leach Liquor | | | 45 | 18 |
| | | | .104 | " | " | " | " | 45 | 20 |
| | | | .099 | D-95 | " | " | " | ~0 | 250 |
| | | | .091 | " | " | " | " | ~0 | 250 |
| Di(2-ethylhexyl) | A | 241 | 0.100 | D-95 | | Water | | 1 | 10 |

Table 7 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

| Organic Phase | | | | | Aqueous Phase[a] | | | Loss of Amine | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Concn. | | Fraction Readily | Steady-State |
| Amine | Batch | Mol. Wt. | Init. Concn. M | Diluent | Solute | M | pH | Lost, % of Init. | Loss ppm/aq |
| Di(2-ethylhexyl) | A | 241 | 0.100 | Benzene | Syn. Leach Liquor | | | 18 | 855 |
| | | | .097 | D-95 | " | " | " | 16 | 1650 |
| | | | .100 | $CHCl_3$ | " | " | " | 15 | ~100 |
| C&CCC 15F53 | A | 270 | 0.099 | Benzene | Syn. Leach Liquor | | | 25 | 700 |
| | | | .099 | " | " | " | " | 20 | 800 |
| | | | .196 | D-95 | " | " | " | 25 | 2000 |
| | | | .095 | " | " | " | " | 30 | 1250 |
| | | | .199 | Kerosene | " | " | " | 35 | 4600 |
| | | | .107 | " | " | " | " | | ~5000 |
| Di-n-decyl | C | 298 | 0.099 | Benzene | Water | | | 0 | 0 |
| | C | | 0.100 | Benzene | Syn. Leach Liquor | | | 0 | 0 |
| | F | | .089 | D-95 | " | " | " | 0 | 5 |
| Dilauryl | A | 354 | 0.089 | D-95 | $SO_4$ | 0.4 | 0.42 | 0 | 0 |
| | | | .089 | " | $SO_4$ | 0.4 | 1.25 | 0 | 0 |
| Dilauryl, 50°C | F | | .092 | " | Syn. Leach Liquor (50°C) | | | ~0 | ~0 |
| C&CCC 16F27 | A | 354 | 0.099 | Benzene | Syn. Leach Liquor | | | 25 | 40 |
| | | | .098 | " | " | " | " | 25 | 50 |

Table 7 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

| Organic Phase | | | | | Aqueous Phase[a] | | | Loss of Amine | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Concn. | | Fraction Readily | Steady-State |
| Amine | Batch | Mol. Wt. | Init. Concn. M | Diluent | Solute | M | pH | Lost, % of Init. | Loss ppm/aq |
| **Tertiary** | | | | | | | | | |
| Tri-n-butyl | A | 185 | 0.1 | Benzene | Syn. Leach Liquor | | | | $>2\times10^4$ |
| | | | .102 | " | " | " | " | | $>2\times10^4$ |
| | | | .381 | " | " | " | " | | $>7\times10^4$ |
| | A | | .394 | $CHCl_3$ | " | " | " | | $5\times10^4$ |
| Tri-n-hexyl | A | 270 | 0.100 | D-95 | Water | | | 13 | 0 |
| | A | 270 | 0.094 | Benzene | Syn. Leach Liquor | | | ~15 | ~450 |
| | | | .092 | D-95 | " | " | " | 20 | 1300 |
| | | | .085 | $CHCl_3$ | " | " | " | 0 | < 200 |
| Tri-n-octyl | G | 354 | 0.049 | Benzene | $HNO_3$ | 1 | | 2 | 0 |
| | | | .049 | " | HCl | 1 | | 0 | 0 |
| | | | .049 | " | $H_2SO_4$ | 1 | | 1 | < 15 |
| | | | .049 | " | $H_3PO_4$ | 1 | | ~8 | < 25 |
| | | | .054 | " | $Na_2CO_3$ | 1 | | 0 | 0 |
| | | | 0.074 | " | $SO_4$ | 0.2 | 0.63 | 1 | 0 |
| | | | .074 | " | $SO_4$ | 0.2 | 1.39 | 3 | 0 |
| | | | .092 | " | $SO_4$ | 0.4 | 0.42 | 2 | 0 |
| | | | .092 | " | $SO_4$ | 0.4 | 1.25 | 2 | 0 |

Table 7 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

| Organic Phase | | | | | Aqueous Phase[a] | | | Loss of Amine | |
|---|---|---|---|---|---|---|---|---|---|
| Amine | Batch | Mol Wt. | Init. Concn. M | Diluent | Solute | Concn. M | pH | Fraction Readily Lost, % of Init. | Steady-State Loss ppm/aq |
| Tri-n-octyl | G | 354 | 0.0925 | Benzene | Syn. Leach Liquor | | | 2 | 0 |
| | D | | .088 | D-95 | " | " | " | 4 | 5 |
| | D | | .084 | (d) | " | " | " | 3 | 15 |
| Tri-n-octyl, 50°C | F | | .093 | D-95 | " | " | " (50°C) | 12 | 2 |
| Tri-n-decyl | D | 438 | 0.095 | Kerosene | Syn. Leach Liquor | | | 6 | 25 |
| Di-n-butyllauryl | A | 298 | 0.100 | D-95 | Syn. Leach Liquor | | | 7 | 65 |
| Di-n-hexyllauryl | A | 354 | 0.100 | D-95 | Syn. Leach Liquor | | | 0 | 0 |
| Methyldi-n-octyl | A | 255 | 0.092 | Benzene | Water | | | 0 | 5 |
| | | | 0.085 | " | $HNO_3$ | 1 | | 0 | 0 |
| | | | .085 | " | HCl | 1 | | 0 | 65 |
| | | | .090 | " | $H_2SO_4$ | 1 | | 2 | 90 |
| | | | .084 | " | $H_3PO_4$ | 1 | | 7 | 800 |
| | | | .085 | " | $Na_2CO_3$ | 1 | | 0 | 0 |
| | | | 0.093 | " | $SO_4$ | 1 | 1.41 | 2 | 15 |

Table 7 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

| Organic Phase | | | | | Aqueous Phase[a] | | | Loss of Amine | |
|---|---|---|---|---|---|---|---|---|---|
| Amine | Batch | Mol. Wt. | Init. Concn. M | Diluent | Solute | Concn. M | pH | Fraction Readily Lost, % of Init. | Steady-State Loss ppm/aq |
| Methyldi-n-octyl | A | 255 | 0.176 | Benzene | $H_2SO_4$ | 0.5 | | 1 | 165 |
| | | | .090 | " | " | 0.5 | | 2 | 165 |
| | | | .092 | D-95 | " | 0.5 | | 6 | 340 |
| | | | .009 | Benzene | " | 0.5 | | 14 | 110 |
| | | | .009 | " | " | 0.5 | | 9 | 110 |
| | | | .090 | " | $SO_4$ | 0.5 | 1.02 | 0 | 90 |
| | | | .090 | " | " | 0.5 | 1.55 | 0 | 80 |
| | | | 0.086 | " | $SO_4$ | 0.2 | 0.63 | 0 | 275 |
| | | | .086 | " | " | 0.2 | 1.39 | 2 | 205 |
| | | | .090 | " | " | 0.1 | ~13. (f) | 0 | 0 |
| | | | 0.084 | " | $H_2SO_4$ | 0.053 | | 11 | 340 |
| | | | .009 | " | " | 0.053 | | | 380 |
| | | | .008 | " | " | 0.053 | | 6 | 410 |
| | | | 0.090 | " | Syn. Leach Liquor | | | ~2 | 150 |
| Methyldi-n-decyl | D | 312 | 0.100 | Benzene | Syn. Leach Liquor | | | 0 | 0 |
| | | | .099 | D-95 | " " " | | | 1 | 15 |
| Methyldilauryl | A | 368 | 0.089 | (b) | $SO_4$ | 0.4 | 0.42 | 0 | 0 |
| | | | .079 | (c) | " | 0.4 | 0.42 | 0 | 0 |
| (β-Hydroxyethyl)-dilauryl | A | 398 | 0.086 | Benzene | Syn. Leach Liquor | | | 0 | 0 |

Table 7 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Tests at Room Temperature except as noted.

a) Aqueous phases were presaturated with the diluent to be used in each test.

b) Diluent was 90% D-95, 10% isoamyl alcohol.

c) Diluent was 83% D-95, 17% capryl alcohol.

d) Diluent was 50% kerosene, 50% D-95.

e) Composition of the synthetic leach liquor:

| Ion: | Fe | Al | F | $PO_4$ | $SO_4$ |
|---|---|---|---|---|---|
| g/liter: | 5.8 | 3.3 | 1.7 | 2.0 | 50. |
| pH: | 0.7-0.8 | | | | |

f) Aqueous phase contained 0.1M $Na_2SO_4$ + 0.1M NaOH.

g) Precipitate formed, presumably containing the amine.

million parts of aqueous raffinate. The latter is characteristic of each system, and should be directly useful in process design. The initial rapid loss depends on the purity of the amine sample, and will be significant for process design only to the extent that the purity of the laboratory samples is typical of the purity to be expected of the reagent when obtained in production quantities.

It should be noted that the validity of the foregoing assumptions has not been rigorously proved even for the few amines which have been studied most. The fundamental studies of the amine solutions which are in progress should help to elucidate this. Meanwhile, the quantities tabulated furnish at the least a concise empirical summary of the total losses actually measured.* It is fortunate that most of those individual amines which are likely to be of interest for process design showed little of the rapid initial loss, so that the steady-state losses found for those can be used with little concern about the theoretical interpretation.

Most of the amines listed were tested for loss to a "synthetic leach liquor" which contained iron, aluminum, fluoride, phosphate, and sulfate (see footnote (e), Table 7). In addition, several were tested for loss to reagent solutions under various conditions, the variables including the anion present in the aqueous phase, its concentration, the pH, the temperature, the initial amine concentration in the organic phase, and the diluent used. The resulting data, together with those from recycle extractions and observations of the screening tests, indicate the following general relationships:

The loss of free amine was low, either to water or to basic solution. The loss of amine sulfate (i.e., amine equilibrated with acidic sulfate solution) was greatest to the most dilute acid solution, decreasing with increasing acid concentration and also decreasing with increasing pH. The loss of amine salt to dilute mineral acids was least to nitric acid, and was greater to hydrochloric, sulfuric, and phosphoric acids in that order.

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*Discordant results were obtained with Armeen 2-8, which should consist principally of di-n-octylamine but may contain significant quantities of other compounds. These tests will be repeated with pure di-n-octylamine.

Hydrocarbon diluents were used in most of the tests, the loss of amine sulfate being least from benzene, somewhat greater from Amsco D-95 (a mineral spirit of high aromatic content), and still greater from kerosene. Much less amine was lost when chloroform was used as the diluent (cf. comparison of benzene and chloroform in the uranium extraction screening tests, Section A). The amount of amine lost depended little if at all on the initial amine concentration, over the range up to at least 0.2M. At still higher concentrations, the loss may be somewhat higher, as a higher loss rate was indicated in a few tests with amines at 0.5M. (These tests were made primarily to eliminate the possibility that the high initial losses, discussed above, might be attributable to near-saturation of the organic phase.)

Only preliminary tests have been made of the effect of temperature; the loss of tri-n-octyl- and of dilaurylamine was not increased when the temperature was raised from about 25° to 50°C (cf. effect of temperature on uranium extraction, Section E).

For each general type of amine tested, the losses of the individual amines to a given solution were related primarily to their molecular weights. Amines of different types showed considerable variation, the losses being generally greater with tertiary than with secondary amines, and greater with a shorter, branched compound than with a longer straight-chain compound, of the same or even higher molecular weight. For example, the loss from Amsco D-95 solution to the synthetic leach liquor was about the same with di(2-ethylhexyl)amine (mol. wt. 241) as with di-n-heptylamine (213), and was greater with the highly-branched secondary amine C&CCC 15F53 (270). Losses were slightly greater with methyldi-n-octyl- and methyldi-n-decylamine than with di-n-octyl- and di-n-decylamine, in spite of the increased size of the molecules, and loss with the symmetrical tri-n-hexylamine (270) was greater than with methyldi-n-octylamine (255). Even with due consideration for such variations, however, the losses from Amsco D-95 to the synthetic leach liquor used in these tests can be generalized as being usually greater than 100 ppm with amines containing 16 carbon atoms or less and usually less than 20 ppm with amines containing 20 carbon atoms or more. The relative importance of such losses can be illustrated by comparison with the amount of uranium to be produced from a typical liquor. If the pregnant liquor contained 1 g U/l, 100 ppm loss of amine in the raffinate would be equivalent to a loss of 0.1 pound per pound of uranium, and 20 ppm, 0.02 pound per pound. With di-n-decyl-,

dilauryl-, tri-n-octyl-, trilauryl-, methyldilauryl-, or di-n-hexyllaurylamine, a loss to such a liquor would be 0.005 pound or less per pound of uranium produced. For comparison, when these amines are used at a concentration of 0.1M, this loss by distribution to the aqueous phase will be less than the loss which would be caused by entrainment, if only 0.2 ml of the organic phase remained entrained in each liter of the raffinate.

## E. EFFECTS OF EXTRACTION VARIABLES ON URANIUM EXTRACTION

### Effect of Amine Concentration

In general, when a solvent used in liquid-liquid extraction consists of a reagent dissolved in an inert diluent, the extraction coefficient varies with the reagent concentration in a manner which depends on the stoichiometry of the extracted complex. For example, if a metal ion $M^+$ is extracted by a reagent $X^-$ in the form MX, the extraction coefficient $E_a^o$ will be directly proportional to the reagent concentration, $(X^-)$. Similarly, for $M'X_2$, $E_a^o \propto (X^-)^2$, and for $M''X_3$, $E_a^o \propto (X^-)^3$, etc. The evaluation of this relationship for a reagent is important, as it determines the extent to which the effective extraction coefficient in a particular process can be adjusted by adjustment of the solvent phase.

Uranium extraction by several of the amines was examined at two or more amine concentrations, from sulfate solutions at about pH 1. When the excess of amine was sufficient to avoid saturation effects, the extraction coefficient was found to be directly proportional to the amine concentration within the analytical accuracy. This is illustrated in Figure 2, which shows extractions by dilaurylamine in Amsco D-95 from three sulfate liquors. There is considerable scatter shown, as must be expected since measurement of such high extraction coefficients depended on the fluorimetric analysis of very low concentrations of uranium in the raffinates. In spite of the scatter, the range is sufficient to establish clearly that the curves are straight rather than parabolic or of higher order.

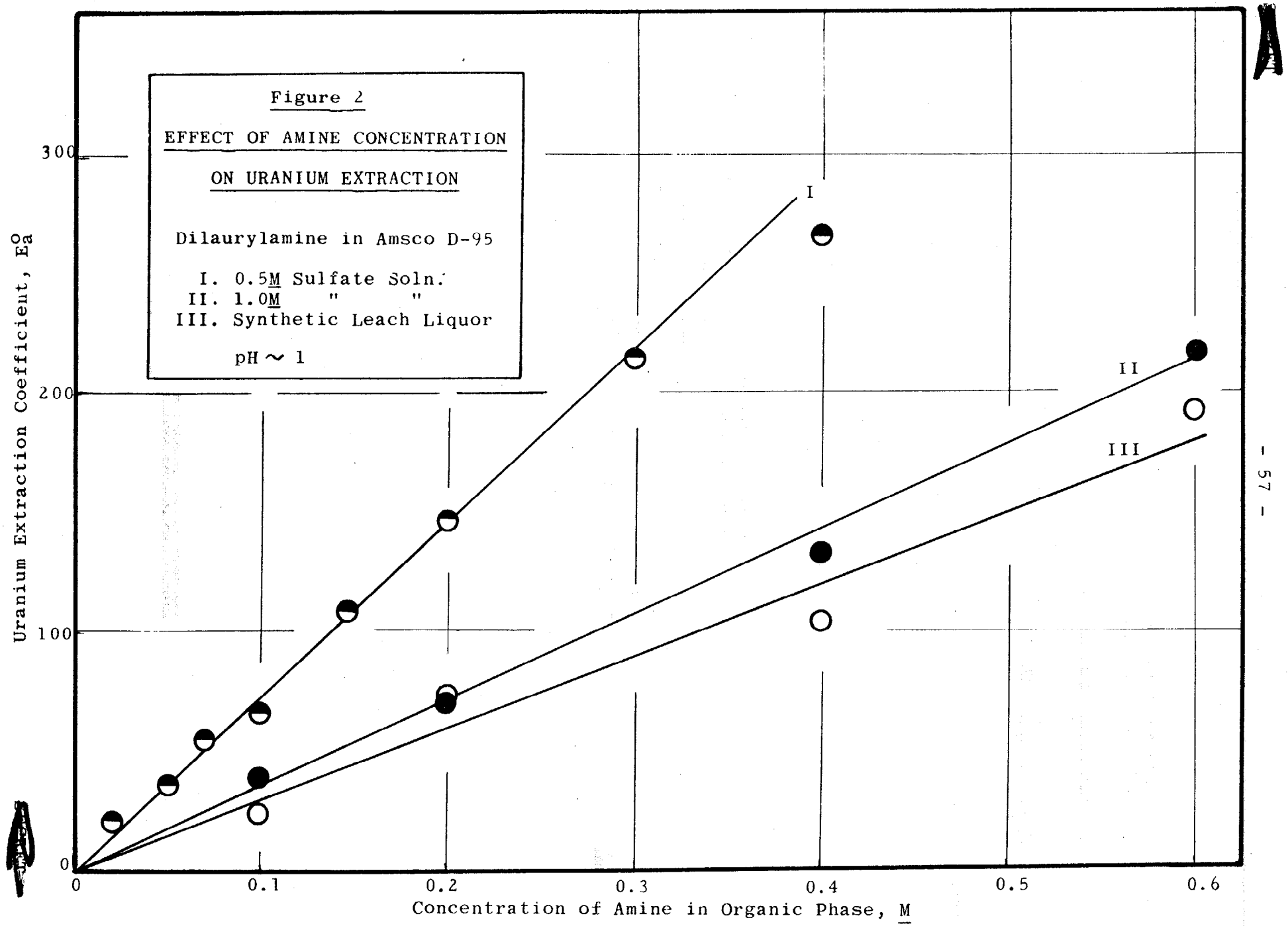
Figure 2
EFFECT OF AMINE CONCENTRATION
ON URANIUM EXTRACTION
Dilaurylamine in Amsco D-95
I. 0.5M Sulfate Soln.
II. 1.0M " "
III. Synthetic Leach Liquor
pH ~ 1
Uranium Extraction Coefficient, $E_a^o$
300
200
100
0
I
II
III
0
0.1
0.2
0.3
0.4
0.5
0.6
Concentration of Amine in Organic Phase, M

Evidence has been found in other types of tests that, at least near pH 1, the amine sulfates may exist in hydrocarbon diluents in some form (e.g., a colloidal dispersion) in which the amine activity is constant over a wide range of nominal concentrations. If this is correct for the amine sulfate and also for the extracted uranium, the true extraction coefficient should be constant over the same range regardless of the stoichiometry of the complex formed, and the nominal coefficient as calculated should appear to be directly proportional to the nominal amine concentration. This and related effects are discussed more completely in Appendix C.

## Effect of Temperature

The extraction of uranium from 1M sulfate solutions at pH 1 was investigated over a temperature range of 20-50°C using 0.1M solutions of four different secondary and tertiary amines in Amsco D-95. As may be observed from Figure 3, the extraction coefficients decreased as the temperature was raised with all four of the amines tested. In most cases, the loss in extraction efficiency was appreciable, but fortunately the amines are effective enough as extractants so that even at 50°C the extraction coefficients should be sufficient for a practicable solvent extraction operation.* Attempts to measure extraction at temperatures below those studied were unsuccessful. At 10°C, for example, in each case the amine salt was precipitated from the organic diluent.

## Effect of Sulfate Concentration and pH

Uranium extraction from sulfate solution was found to be sensitive to both the sulfate content and the pH of the aqueous phase. In general, the effects were similar to those found in anion exchange sorption of uranium from similar liquors, the extractions being higher at low sulfate concentration and at high pH, at least up to about pH 2. (The analogy of extraction by amines with anion exchange sorption is discussed in Appendix C.) Test results with several amines are summarized in Table 8 and illustrated by Figures 4, 5 and 6. Except where otherwise

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*It appeared that phase separation was more rapid at the higher temperatures, although no quantitative measurements were made (see also Sections B and F).

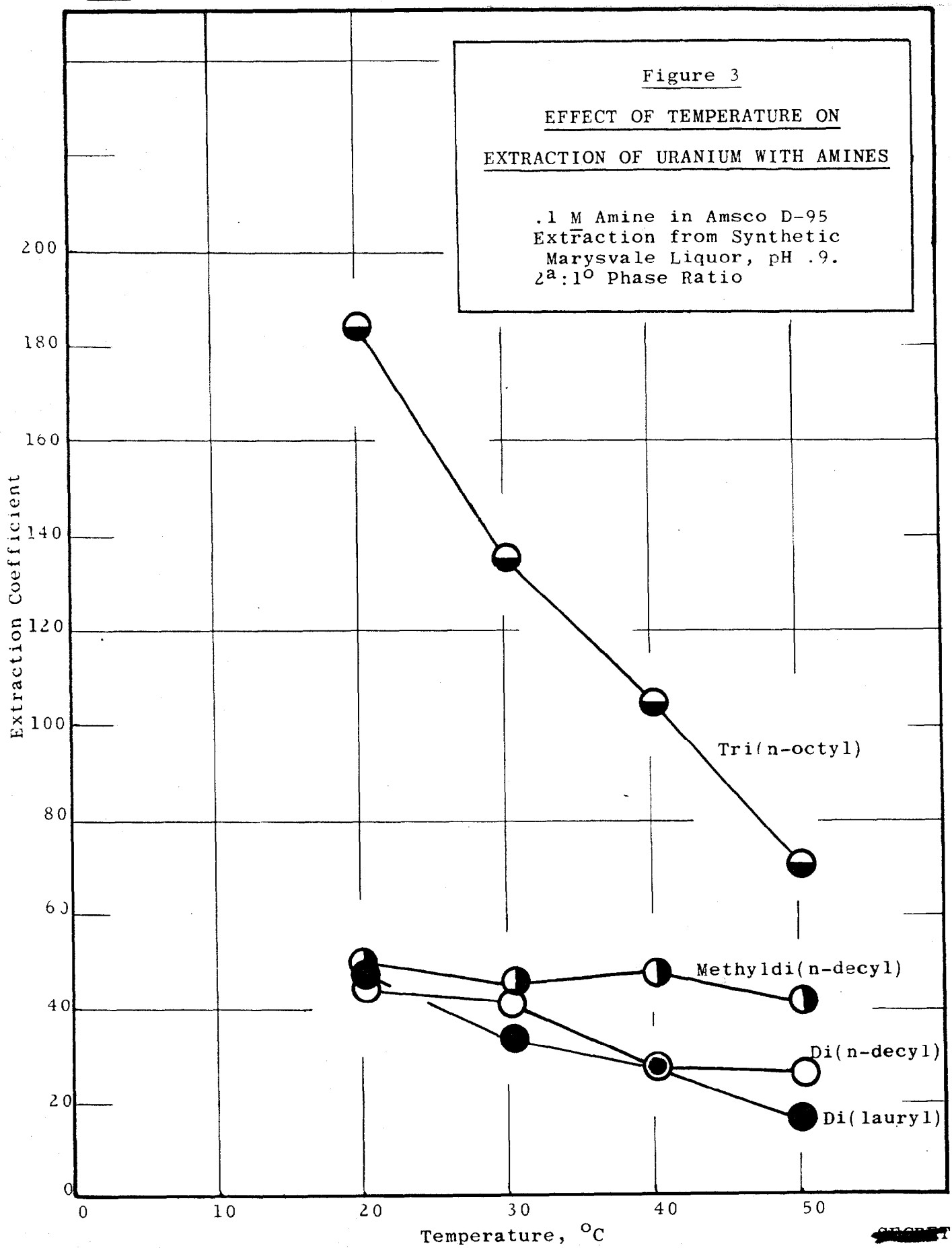


Figure 3
EFFECT OF TEMPERATURE ON
EXTRACTION OF URANIUM WITH AMINES
.1 M Amine in Amsco D-95
Extraction from Synthetic
Marysvale Liquor, pH .9.
2a:1o Phase Ratio
Extraction Coefficient
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
Temperature, °C
Tri(n-octyl)
Methyldi(n-decyl)
Di(n-decyl)
Di(lauryl)

Table 8

EFFECT OF SULFATE CONCENTRATION AND pH ON URANIUM EXTRACTION

| Amine | Init. $SO_4$ Concn., M | pH | | Uranium Extraction Coeff., $E_a^o$ |
|---|---|---|---|---|
| | | Initial | Final | |
| Di-n-decyl | 0.1 | 1.0 | 1.1 | 425 |
| | | 1.5 | 2.0 | 770 |
| | | 2.0 | 2.6 | 830 |
| | 0.2 | 0.8 | | 120 |
| | | 1.5 | 1.7 | 390 |
| | | 2.0 | 3.0 | 570 |
| | 0.5 | 0.4 | | Emul. |
| | | 1.1 | 1.2 | 70 |
| | | 1.9 | 2.3 | 220 |
| | 1.0 | 0.2 | | Emul. |
| | | 1.1 | | 20 |
| | | 2.0 | 2.1 | 75 |
| | 1.5 | 0.05 | | Emul. |
| | | 1.0 | 1.1 | 8 |
| | | 2.1 | 2.2 | 40 |
| | 2.0 | < 0 | | Emul. |
| | | 1.0 | 1.0 | 5 |
| | | 2.0 | | 25 |
| Dilauryl | 0.1 | 1.0 | 1.1 | 370 |
| | | 1.5 | 1.9 | 650 |
| | | 2.0 | | 630 |
| | 0.2 | 0.8 | 0.8 | 90 |
| | | 1.5 | 1.8 | 350 |
| | | 2.0 | 2.6 | 460 |
| | 0.5 | 0.4 | 0.5 | 20 |
| | | 1.1 | 1.2 | 60 |
| | | 1.9 | 2.3 | 170 |

Table 8 (Cont'd.)

EFFECT OF SULFATE CONCENTRATION AND pH ON URANIUM EXTRACTION

| Amine | Init. $SO_4$ Concn., M | pH Initial | pH Final | Uranium Extraction Coeff., $E_a^o$ |
|---|---|---|---|---|
| Dilauryl (Cont'd.) | 1.0 | 0.2 | | Emul.. |
| | | 1.1 | 1.2 | 15 |
| | | 2.0 | 2.1 | 60 |
| | 1.5 | 0.05 | | Emul. |
| | | 1.0 | 1.2 | 8 |
| | | 2.1 | 2.2 | 30 |
| | 2.0 | < 0 | | Emul. |
| | | 1.0 | 1.1 | 4 |
| | | 2.0 | 2.1 | 20 |
| Methyldi-n-decyl | 0.5 | 0.4 | 0.4 | 10 |
| | | 1.0 | 1.1 | 40 |
| | | 1.8 | 2.0 | 120 |
| | 1.0 | 0.4 | 0.5 | 7 |
| | | 1.0 | 1.1 | 20 |
| | | 1.8 | 2.0 | 50 |
| Tri-n-octyl | 0.1 | 1.0 | 1.2 | 800 |
| | | 1.5 | 1.7 | 1100 |
| | | 2.0 | 2.5 | 60 |
| | 0.2 | 0.8 | 0.8 | 300 |
| | | 1.5 | 1.7 | 750 |
| | | 2.0 | 2.2 | 290 |
| | 0.5 | 0.4 | 0.5 | 40 |
| | | 1.1 | 1.2 | 160 |
| | | 1.9 | 2.1 | 210 |
| | 1.0 | 0.2 | 0.2 | 8 |
| | | 1.0 | 1.1 | 60 |
| | | 1.9 | 2.0 | 110 |

Table 8 (Cont'd.)

EFFECT OF SULFATE CONCENTRATION AND pH

ON URANIUM EXTRACTION

| Amine | Init. $SO_4$ Concn., M | pH | | Uranium Extraction Coeff., $E_a^o$ |
|---|---|---|---|---|
| | | Initial | Final | |
| Tri-n-octyl (Cont'd.) | 1.5 | 0.05 | 0.2 | 2 |
| | | 1.0 | 1.1 | 30 |
| | | 2.1 | 2.2 | 50 |
| | 2.0 | < 0 | < 0 | 1 |
| | | 1.0 | 1.0 | 10 |
| | | 2.0 | 2.1 | 40 |

Extraction Conditions:

Uranium head, 1 g U/l.
Phase ratio, 2 aqueous : 1 organic.
Amine concentration, 0.1M.
Diluent, Amsco D-95.

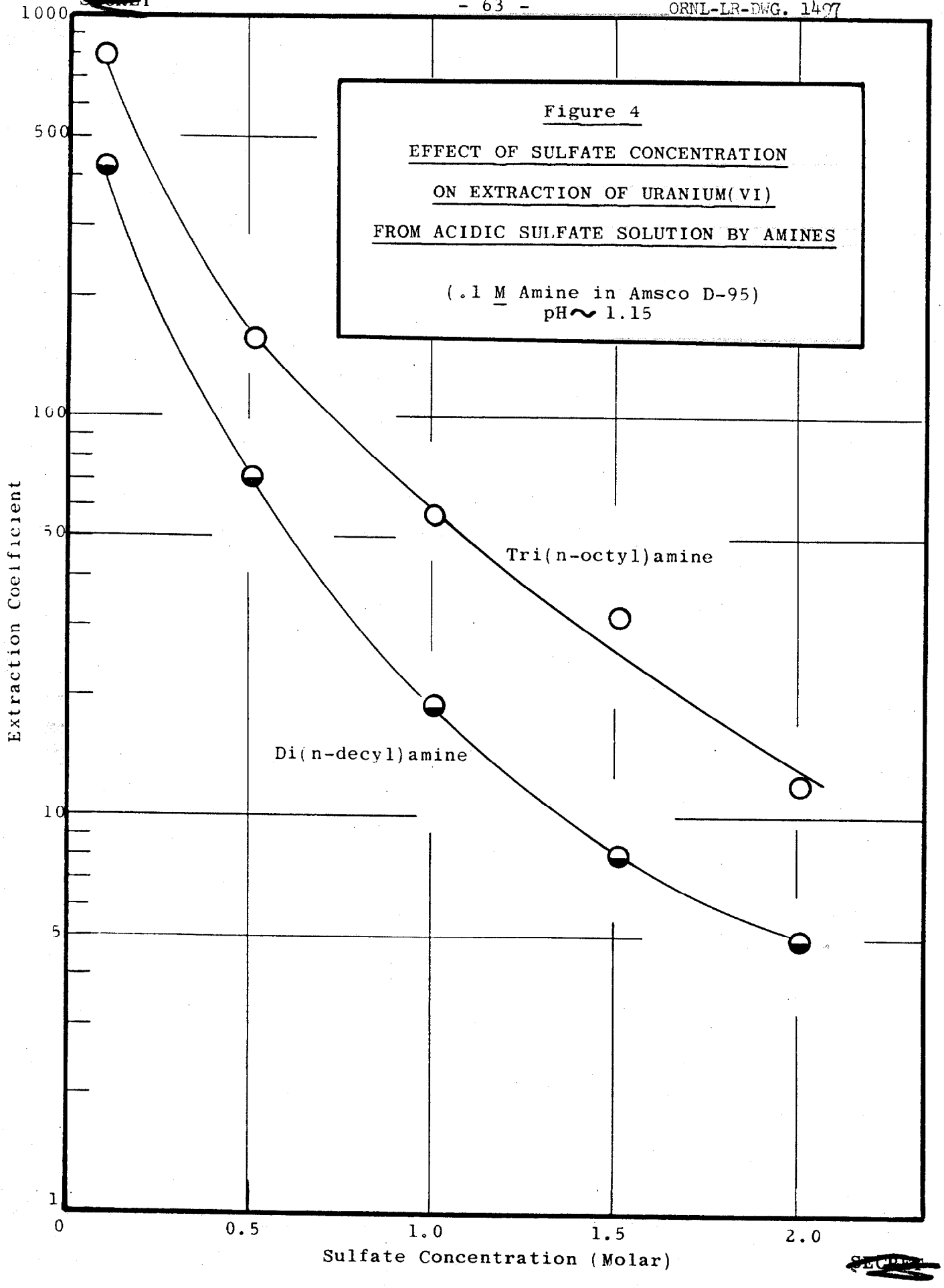



Figure 4

EFFECT OF SULFATE CONCENTRATION ON EXTRACTION OF URANIUM(VI) FROM ACIDIC SULFATE SOLUTION BY AMINES

(.1 M Amine in Amsco D-95)
pH ~ 1.15

ORNL-LR-DWG. 1498

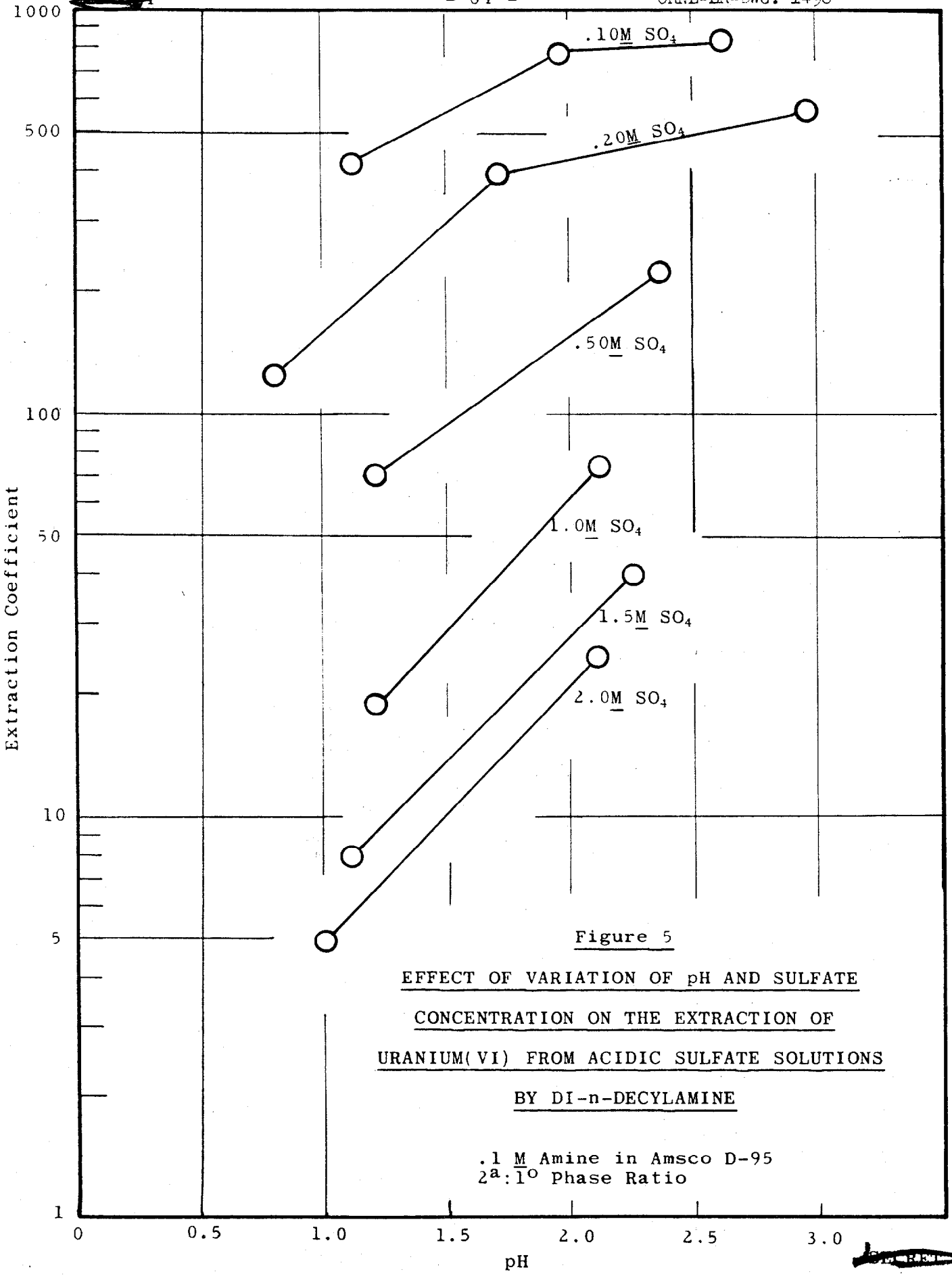



Figure 5

EFFECT OF VARIATION OF pH AND SULFATE CONCENTRATION ON THE EXTRACTION OF URANIUM(VI) FROM ACIDIC SULFATE SOLUTIONS BY DI-n-DECYLAMINE

.1 M Amine in Amsco D-95
$2^a:1^o$ Phase Ratio

ORNL-LR-DWG. 1499

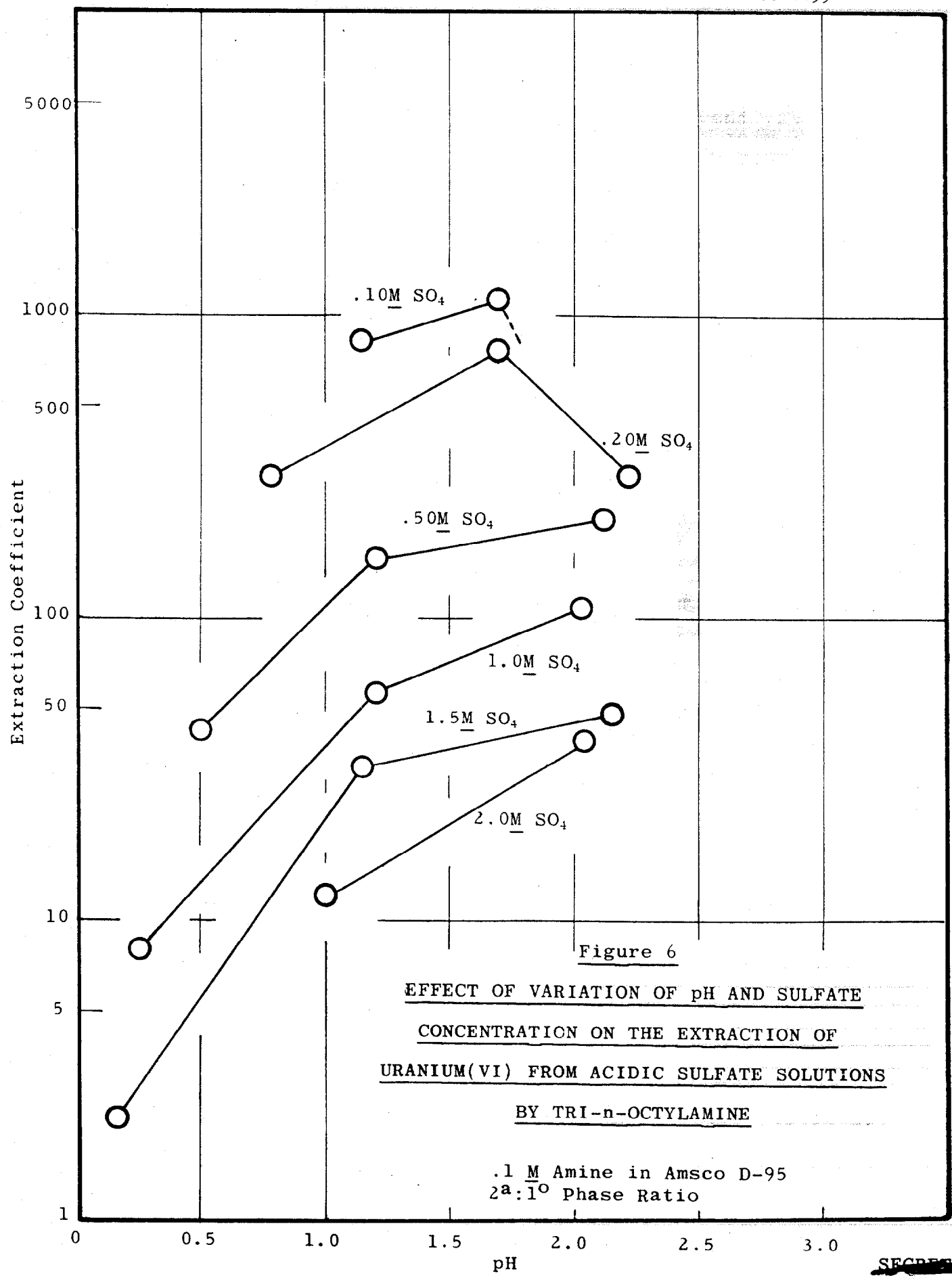



Figure 6

EFFECT OF VARIATION OF pH AND SULFATE CONCENTRATION ON THE EXTRACTION OF URANIUM(VI) FROM ACIDIC SULFATE SOLUTIONS BY TRI-n-OCTYLAMINE

.1 M Amine in Amsco D-95
$2^a:1^o$ Phase Ratio

specified, the amines were used at a concentration of 0.1M in Amsco D-95; the aqueous solutions consisted of uranyl sulfate with sulfuric acid or mixtures of sulfuric acid and ammonium sulfate.

High extraction coefficients were obtained with 0.1M amines in the range of liquor compositions typical of uranium ore-processing operations, e.g., sulfate concentration below 1M and pH at or a little above 1. The coefficients increased as the pH was raised to about 1.5, then began to level off, especially when the sulfate concentration was very low. At a little above pH 2, the coefficients obtained with tri-n-octylamine dropped sharply, while the secondary amines tested remained effective at a somewhat higher pH level; the difference may be a function of the individual base strengths. In the other direction, extraction was decreased as the acidity was increased, the coefficients being about one-third as great at pH 0.4-0.5 as at pH 1.

The effect of varying sulfate concentration (with the pH held constant at, say, 1) was similar to that found in anion exchange sorption from very dilute uranium solutions, i.e., sorption when the resin was far from saturation with uranium (Y-816, p. 61).[7] With dilaurylamine at pH ~1.2, the coefficients rose from about 20 at 1M sulfate to 60 at 0.5M, and similarly with tri-n-octylamine, from about 60 at 1M to 160 at 0.5M. At pH 0.5 and 0.5M sulfate, the coefficients obtained with these two amines were about 20 and 40, respectively. Thus, even at pH levels considerably below 1, good extraction could be maintained if the sulfate concentration could also be kept low. (This observation applies, of course, only to sulfate solutions, without significant concentrations of other anions.) It may also be noted that if sulfate concentrations somewhat above 1M were encountered, reasonable extraction coefficients could be maintained by increasing the concentration of amine in the organic phase (see above).

## Effect of Other Anions

Since minerals containing phosphate and fluoride are frequently found in uranium ores, these anions are common contaminants in most of the sulfuric acid leach liquors. Solvent extraction processing of the liquors may also add other anions to the system as a natural consequence of the operation, e.g., if acid chloride or nitrate solutions were used in the stripping section, hydrochloric or nitric acid would be returned to the extraction system in quan-

tities equivalent to that of the amine (i.e., as $R_xNH_{3-x}HCl$ or $R_xNH_{3-x}HNO_3$ - see Section H).* For these reasons each of the anions, $Cl^-$, $F^-$, $NO_3^-$, and $PO_4^{\equiv}$, has been examined as to its effect at low concentrations on the extraction of uranium from sulfate solutions; the results from these tests are listed in Table 9 and depicted graphically in Figures 7 and 8.

Since dilute acid nitrate solutions are very effective stripping agents, i.e., the amine prefers nitric acid to the uranium complex, it is not surprising that the addition of small quantities of nitrate to the acid sulfate liquors will cause a particularly strong adverse effect on the extraction of uranium. With the liquors tested, addition of only 0.05M nitrate ion decreased the uranium extraction coefficient for tri-n-octylamine from 44 to 1. Thus, if acid nitrate solutions were used as stripping agents, it would be necessary to remove the nitrate from the organic phase, e.g., by a basic scrub, prior to its return to the extraction cycle.

Acidic chloride solutions are less effective than nitrate solutions in stripping uranium and, conformably, the effect of chloride on uranium extraction though significant is less than that for nitrate. Scrubbing of the organic phase after hydrochloric acid stripping may or may not be advisable, depending upon the balance between the costs for increased extraction capacity and the costs for scrubbing. Under the conditions of the experiments, the effect from fluoride was generally similar to that from chloride. Initial small additions of phosphate for some unknown reason caused a slight increase in the extraction coefficient. Further addition gave a deleterious effect though not so severe as with the other anions tested. In reference to the results with fluoride and phosphate, it should be noted that the experiments described here were made with "pure" uranium solutions and that different results would be expected with actual leach liquors. As shown previously, both of these ions can complex strongly with other extractable metals such as iron or molybdenum and, thus, prevent their take-up by the organic solvent. The total effect can be one of benefit both to the extraction coefficient and to the selectivity of the uranium separation.

Again, as might be predicted from stripping tests (Section H), the physical performance of the straight-chain secondary amines such as dilaurylamine was poor when nitrate or chloride ions were added to the system. Phase separation was slow, apparently due to the precipitation of the amine

Table 9

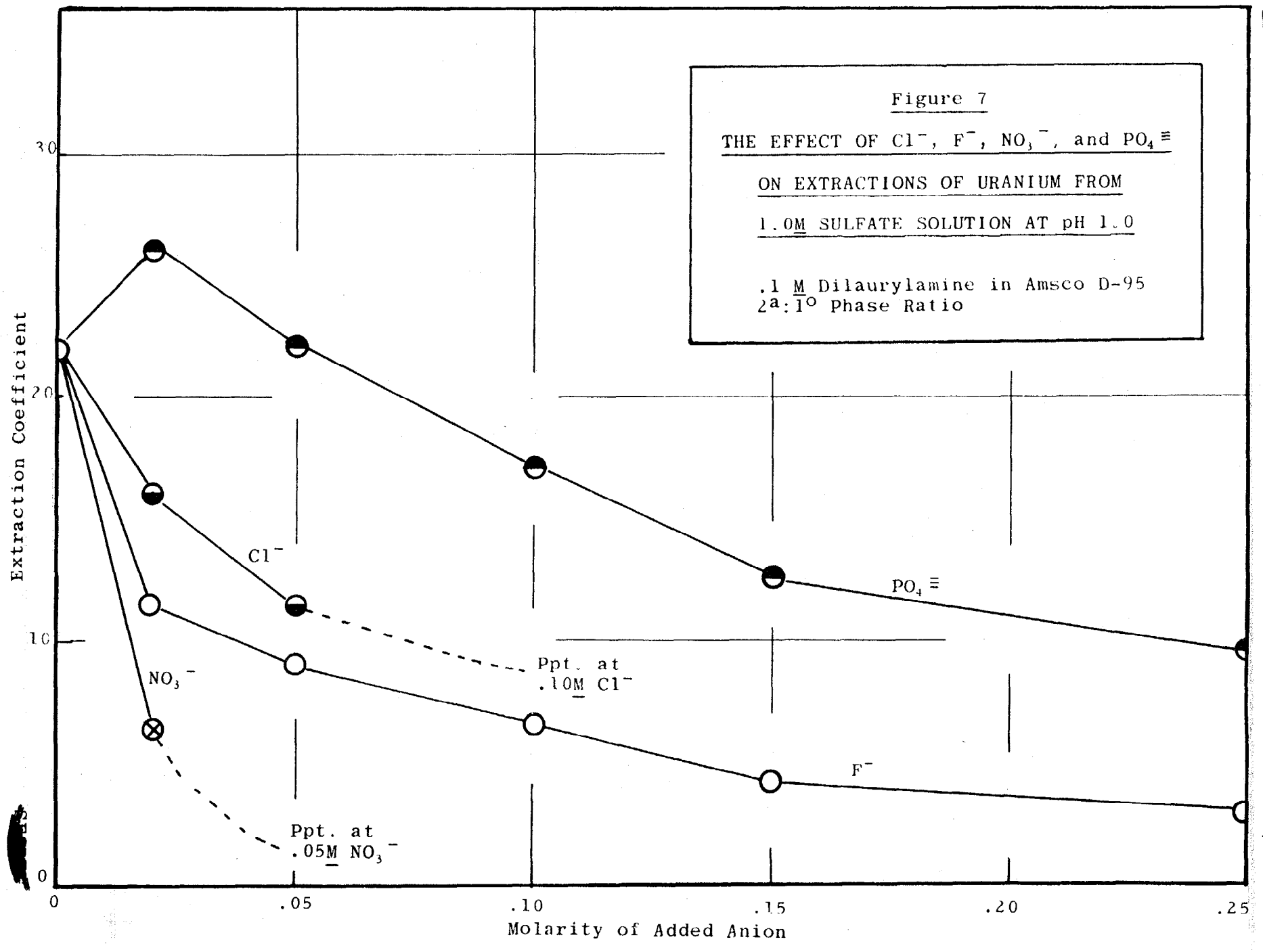
EFFECT OF VARIOUS ANIONS ON THE EXTRACTION OF URANIUM(VI) FROM ACIDIC SULFATE SOLUTION

| Amine (0.1M) | Concn. of Added Anion (Molar)* | Extraction Coefficient $Cl^-$ | $F^-$ | $NO_3^-$ | $PO_4^{\equiv}$ |
|---|---|---|---|---|---|
| Dilauryl | 0 | ---------22---------- | | | |
| " | .02 | 16 | 12 | 6 | 25 |
| " | .05 | 12 | 9 | ** | 20 |
| " | .10 | ** | 7 | ** | 17 |
| " | .15 | ** | 4 | ** | 12 |
| " | .25 | ** | 3 | ** | 10 |
| Tri-n-octyl | 0 | ---------44---------- | | | |
| " | .02 | 32 | 24 | 10 | 55 |
| " | .05 | 18 | 17 | 1 | 36 |
| " | .10 | 10 | 7 | .1 | 22 |
| " | .15 | 6 | 3 | .04 | 15 |
| " | .25 | 2 | 1.0 | .01 | 12 |

Extraction Conditions: Head Solution: 1.0M $SO_4$, 1.0 g U/l, pH 0.93
Phase Ratio: 2 aqueous : 1 organic
Diluent: Amsco D-95.

*Chloride, fluoride, and nitrate added as alkali salts; phosphate added as phosphoric acid.

**Precipitation of some of the amine salt.



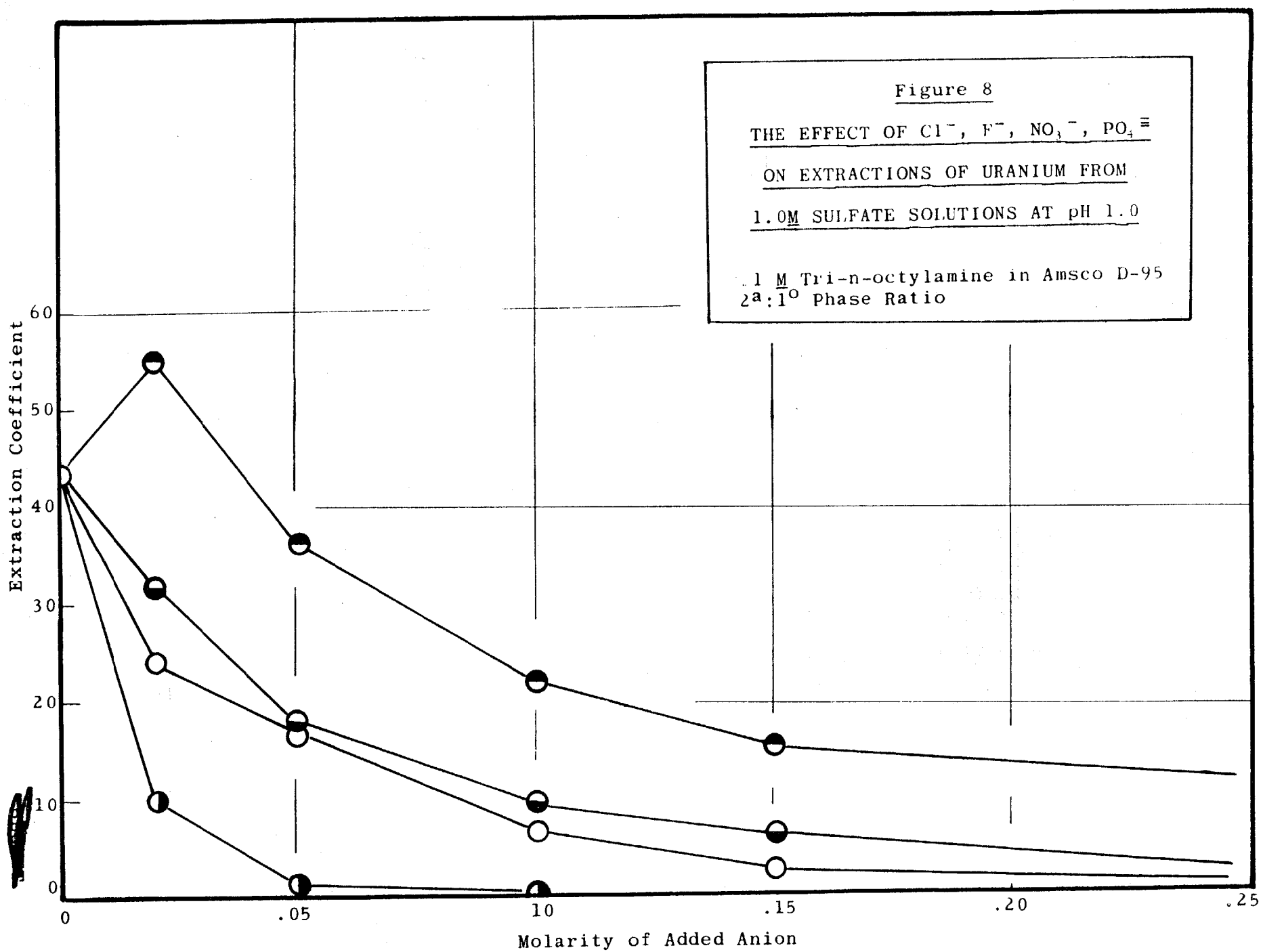


Figure 8
THE EFFECT OF Cl⁻, F⁻, NO₃⁻, PO₄≡
ON EXTRACTIONS OF URANIUM FROM
1.0M SULFATE SOLUTIONS AT pH 1.0
.1 M Tri-n-octylamine in Amsco D-95
2a:1o Phase Ratio
Extraction Coefficient
60
50
40
30
20
10
0
0
.05
10
.15
.20
.25
Molarity of Added Anion

salt which was noted in some cases. The tertiary and branched-chain secondaries were again more tolerant of chloride and nitrate, and phase separation difficulties were not encountered with these reagents.

---

*Chloride is also present in the uranium-bearing acid liquor from the salt roast, acid leach process[8] as a natural result of the process flowsheet which incorporates the recovery of HCl from the roast gases. This HCl is fortified with $H_2SO_4$ and used for the acid leach. As a consequence, the extraction coefficients with the amines from these liquors would be lower than for liquors which contained only sulfate as the anion. The extent of the reduction of coefficient would be dependent upon the amount of chloride present and upon the sulfate/chloride ratio (see Y-818, p. 79 ff.).[7]

---

## F. RATE OF URANIUM EXTRACTION

Qualitative measurements of the rate of uranium extraction into 0.1M di-n-decylamine in Amsco D-95 have been made by contacting this solvent with aqueous uranium sulfate liquor in a separatory funnel for various periods of time, permitting the phases to separate over a period of 25 seconds, and measuring the final uranium concentration in both the aqueous and organic layers. Series of tests were made starting with free amine in the organic phase and also starting with amine sulfate salt, prepared by precontacting the organic phase with an excess of sulfuric acid.

From the data in Table 10, it is apparent that uranium extractions were rapid when either the amine salt or the free amine was used. Coefficients after the shortest time interval studied, 10 seconds shaking time plus 25 seconds for separation, were essentially the same as those after the longest interval, 4 minutes shaking plus 25 seconds for separation. Further, since this was true of the results with both the free amine and the amine salt, it is apparent that the rate of extraction of sulfuric acid will impose no important limitation upon the rate at which uranium is extracted, although the extraction of the acid to form amine sulfate may play an important role in the extraction mechanism (cf. Appendix C).

Table 10

RATE OF URANIUM EXTRACTION

FROM SULFATE SOLUTION

| Contact Time,* Sec. | Extraction Coefficient, $E_a^o$ | |
|---|---|---|
| | (a) Free Amine | (b) Amine Sulfate |
| 10 | 37 | 42 |
| 20 | 40 | 46 |
| 30 | 40 | 50 |
| 60 | 40 | 48 |
| 120 | 36 | 50 |
| 240 | 36 | 47 |

*Plus separation time of 25 seconds for each.

Extraction Conditions:

Aqueous Head, 1 g U/liter, 0.5M $SO_4$, pH 1.0.

Organic Head, (a) 0.1M Di-n-decylamine in D-95.
(b) Same, pre-equilibrated with sulfuric acid.

Phase Ratio, 2 aqueous : 1 organic.

The tests described in Table 10 were made with simple amine or amine salt and pure uranium sulfate solutions. In countercurrent extraction of the relatively impure ore leach liquors, the reagent in the upper extraction stages would not necessarily consist of the simple amine salt only, but could contain in combination, particularly with the secondary amines, a significant quantity of ferric iron which had been extracted in the lower stages. Other tests have shown that the rate of equilibration in uranium extraction may be somewhat slower when the amine is initially in combination with iron. However, the magnitude of this effect in countercurrent extraction of the most highly contaminated liquors tested has not been large.

Although further measurements of the rate of equilibration in larger-scale tests will be needed, the foregoing results indicate that, if adequate mixing is provided, the rate of throughput in a liquid-liquid contactor will be limited by the rate at which the phases separate rather than by the rate at which uranium is transferred.

## Phase Separation

The rate at which the amine-diluent mixtures separate from the aqueous phase is influenced by the characteristics of the amine reagent, the diluent, the aqueous solution and also by the manner and degree of dispersion of the discontinuous phase in the continuous phase and by the temperature of the system. Of the various amines tested, the best general performance has been given by the symmetrical tertiaries such as tri-n-octyl- and tri-n-decyl-, and by the highly branched secondaries such as C&CCC 15F53, 16F27, and ditridecylamine.* With these reagents, the phase separation from a wide variety of synthetic and actual leach liquors (after mixing in a separatory funnel) was rapid (20-30 seconds) when any one of a number of commercial diluents, Amsco D-95, Amsco G, Solvesso 100, 25% D-95 - 75% kerosene was used. The straight chain secondary amines such as di-n-decyl- and dilaurylamine, on the other hand, were not so versatile (see also Section B) and gave rapid separation only when used with certain highly aromatic sol-

*A sample of ditridecylamine was received very recently from the Carbide and Carbon Chemicals Company. It has not been completely examined in other phases of the screening program and, consequently, has not been mentioned in other sections of this report. Tentative results, however, have been promising and it is of particular current interest since it is one of the amines which could probably be made readily available in production quantities.

vents, e.g., Amsco D-95. In these cases, the separation rates were also more dependent upon the composition of the aqueous solution with which they were contacted.

With reagents such as methyldilaurylamine, Armeen 2C and some batches of methyldi-n-decylamine, the phase separations were almost always slow regardless of the solvent used or the composition of the aqueous solution in contact. It was possible, however, in these instances, to speed the rate of separation, usually bringing it into the range of commercial application, by either (1) adding a small quantity of a surface active agent (such as Victawet 12) to the system, (2) modifying the diluent with 2-10% (by volume) of one of the higher alcohols such as capryl and 2-ethylhexanol, or (3) by increasing the temperature. Also, the phase separations were usually more rapid if the phases were originally mixed in a manner similar to that obtained with, e.g., a Rushton-type contactor rather than in a separatory funnel.

The rate and extent of phase disengagement is, of course, an important variable in any solvent extraction system since it determines to a large extent the size, and thus cost, of the extraction contactors and has also a direct effect on the amount of reagent that may be lost from the system through entrainment in the aqueous phase. These factors are especially important in the raw material field when the volumes of liquor are ordinarily high and the concentrations of uranium are usually low. At present, other studies of these variables are being made with various liquors, both on a laboratory and a larger scale. Since the results can vary to some extent with the type of liquors processed, it would also be necessary, in the final analysis of any particular application, to further examine the separations with respect to the day-to-day productions of liquors of the exact type expected to be encountered.

## G. URANIUM LOADING

The loading characteristics of several amine solutions were studied by contacting them with acidic sulfate solutions of varying uranium concentrations. In some tests, the extractions were single-stage. In others, the organic phase was contacted with successive volumes of aqueous solution until the uranium concentration of the raffinate

became essentially equal to that of the head solution. Table 11 and Figure 9 show how loading of the amine phase varied as the uranium concentration of the aqueous phase with which it was in contact was increased. For 0.1M solutions of di-n-decylamine and tri-n-decylamine in Amsco D-95, the loading increased rapidly as the aqueous uranium concentration increased to about one gram per liter, but then leveled off sharply. When the aqueous uranium concentration was in the range of 1-7 g/l, loading of the amine phase was fairly constant at approximately one mole of uranium per 5 moles of amine. Loading values obtained with tri-n-octylamine within the same range of conditions were similar; those with dilaurylamine were slightly lower, about one mole of uranium per 6 moles of amine.

When the concentration of tri-n-octylamine was raised to about 0.6M, the amine phase loaded to 46 g U/l (one mole U per 2.9 moles amine) in equilibrium with a uranium concentration of 6 g/l in the aqueous phase. Dilaurylamine, under essentially the same conditions, loaded to 27 g U/l (one mole U per 5.0 moles amine). In both of these tests, the loaded organic phase became a very thick, viscous syrup.

Changes in sulfate concentration (0.3M to 1.0M) and pH (0.4 to 1.8) of the aqueous solution did not affect the loading to a great extent. Dilaurylamine showed about the same loading in benzene and in chloroform as in Amsco D-95. Tri-n-octylamine showed a little higher loading in benzene and in Amsco D-95 than did dilaurylamine, while its loading in chloroform was similar to that obtained with dilaurylamine. Methyldi-n-decylamine in benzene, under similar conditions, showed about the same loading as did tri-n-octylamine, i.e., approximately one mole uranium per 5 moles amine.

Evidence has been obtained in other tests (see Appendix C) that the limiting uranium sulfate extraction occurs at an amine:uranium ratio of 6 over a wide range of conditions. Although somewhat more variable, the results presented here are in sufficiently close agreement to warrant prediction of the limiting uranium loading available on the basis of a ratio close to 5 or 6, i.e., about 4 or 5 grams uranium per liter for each 0.1 mole of amine per liter, over most of the range of conditions examined.

Table 11

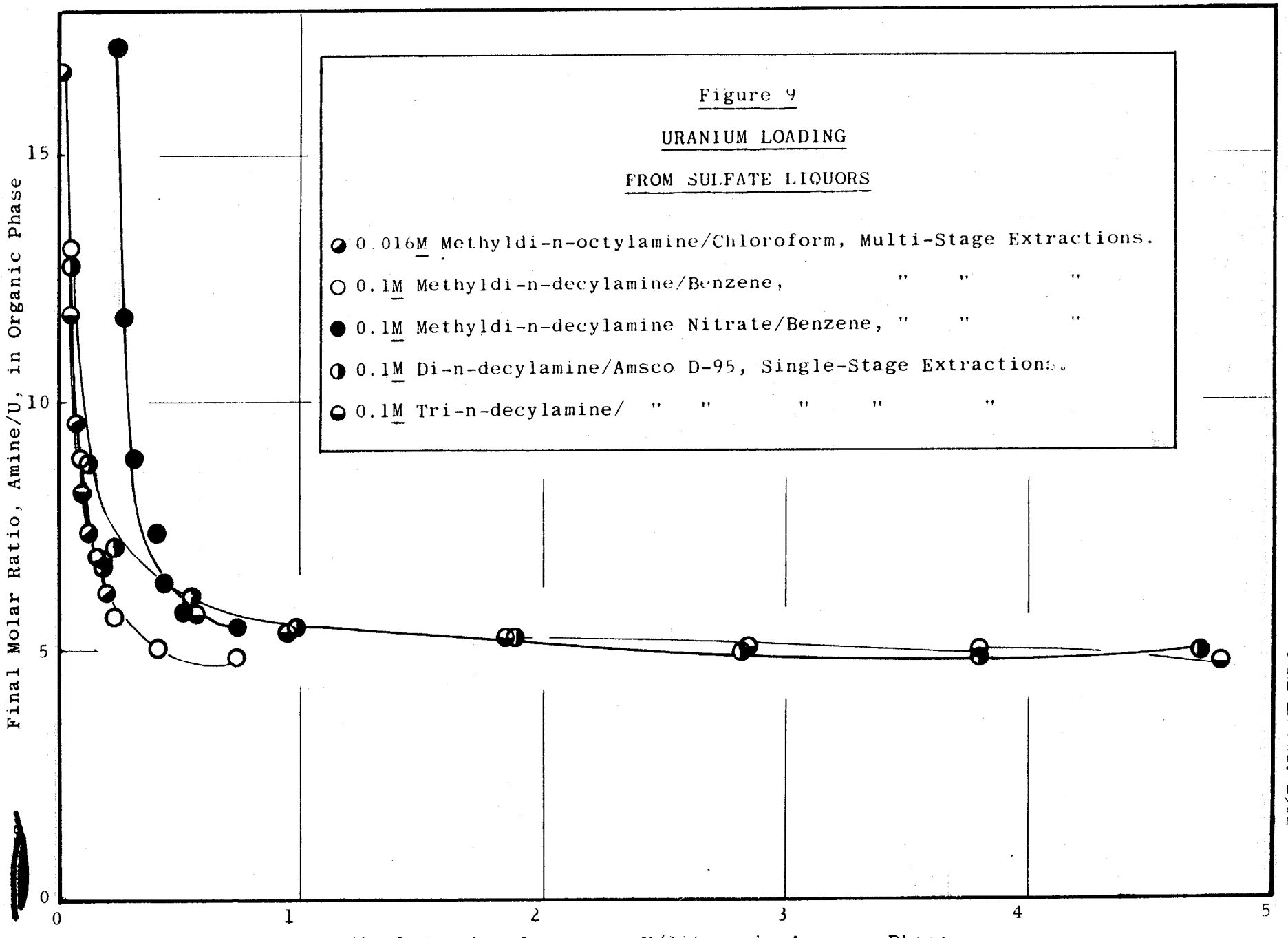
URANIUM LOADING FROM SULFATE SOLUTIONS

| Amine Concn. M | Diluent | Head Solution U g/l | Head Solution $SO_4$ M | Head Solution pH | Results with Tri-n-octylamine: Final U, g/l Aq. | Results with Tri-n-octylamine: Final U, g/l Org. | Results with Tri-n-octylamine: Moles Amine / Mole U Org. | Results with Dilaurylamine: Final U, g/l Aq. | Results with Dilaurylamine: Final U, g/l Org. | Results with Dilaurylamine: Moles Amine / Mole U Org. |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.1[a] | Benzene | 1.0 | 0.5 | 1.0 | 1.00 | 4.79 | 4.7 | 1.03 | 3.84 | 5.9 |
| " | Chloroform | " | " | " | 1.04 | 3.35 | 6.6 | 1.04 | 3.59 | 6.3 |
| " | Amsco D-95 | " | " | " | 1.01 | 4.46 | 4.9 | 0.98 | 3.54 | 6.4 |
| " | " | 0.1[b] | " | " | 0.100 | 2.55 | 8.7 | 0.100 | 2.96 | 7.6 |
| " | " | 3.0[c] | " | " | 3.00 | 4.47 | 4.9 | 2.93 | 4.05 | 5.6 |
| 0.6 | " | 6.0 | " | " | 5.60 | 46.[d] | 2.9 | 5.77 | 27.[d] | 5.0 |
| 0.1[a] | " | 1.0 | 0.3 | " | 0.99 | 4.62 | 4.7 | 0.99 | 3.88 | 5.8 |
| " | " | " | 1.0 | " | 1.03 | 4.13 | 5.4 | 0.98 | 3.40 | 6.7 |
| " | " | " | 0.5 | 0.4 | 1.00 | 3.56 | 6.2 | | | |
| " | " | " | " | 1.8 | 1.04 | 4.00 | 5.5 | 0.98 | 3.63 | 6.3 |

a) Exact concentration: $Oct_3N$, 0.093M; $Lr_2NH$, 0.095M.
b) Phase ratio per stage, aq:org = 13.3.
c) " " " " , aq:org = 1.67.
d) Organic Phase very thick and viscous.

Head Solutions: Uranyl sulfate, sodium sulfate, and sulfuric acid to concentrations and pH shown.

Extraction Conditions: Organic phase equilibrated with 3 successive portions of head solution, at phase ratio of aq:org = 4 (except as noted) in each stage. Third-stage uranium analyses are shown; 3rd-stage pH was the same as head pH.



## H. URANIUM STRIPPING

In the development of a completely successful solvent extraction system, the operational and economic considerations in the stripping step are ordinarily as important as in the extraction cycle. Accordingly, it has been encouraging to find that effective stripping of uranium from the amine-diluent mixtures may be accomplished with several low-cost reagents. Similar to the anion resin systems, good results have been obtained with dilute solutions of nitric acid, hydrochloric acid, nitric acid plus nitrate salt, hydrochloric acid plus chloride salt, sodium carbonate and ammonium carbonate. In addition, since the extractant in this case is a liquid, efficient stripping can be also obtained by direct precipitation of uranium from the organic phase using either sodium or ammonium hydroxide.

Although an exact understanding of the fundamental factors governing the extraction and stripping operations must await the completion of further studies, it is possible to explain the observations made thus far on the basis of several postulated reaction mechanisms, as discussed in Appendix C. (As usual, it would be understood that these postulations may be neither complete nor exclusively correct.) In the extraction step, it may be assumed that essentially all of the free amine is first converted to the amine sulfate salt, and that the extraction of uranium is accomplished by reactions of this salt with the uranium sulfate complexes in the aqueous liquor to form uranium-amine-sulfate complexes in the organic phase. When, for example, a secondary amine such as di-n-decyl- or dilauryl-amine, $R_2NH$, is used, a possible uranium-amine-sulfate complex might be $(R_2NH_2)_2UO_2(SO_4)_2$.

When either sodium or ammonium hydroxide is used as the stripping agent, the uranium is precipitated from the organic phase as the diuranate. Simultaneously, both the amine combined with uranium and the excess amine salt are converted to the amine hydroxide or the free amine, which remains dissolved in the organic diluent and may be directly recycled to the extraction step.

$$2(R_2NH_2)_2UO_2(SO_4)_2 + 10NaOH = 4R_2NH_2OH + Na_2U_2O_7 + 4Na_2SO_4 + 3H_2O \quad (1)$$

$$(R_2NH_2)_2SO_4 + 2NaOH = 2R_2NH_2OH + Na_2SO_4 \quad (2)$$

$$R_2NH_2OH \longrightarrow R_2NH + H_2O \quad (3)$$

Sodium carbonate stripping will also produce the free amine and, in this case, the uranium is dissolved into the aqueous solution as the soluble carbonate complex, i.e.,

$$(R_2NH_2)_2UO_2(SO_4)_2 + 5Na_2CO_3 + 2H_2O = 2R_2NH_2OH + Na_4UO_2(CO_3)_3 + 2Na_2SO_4 + 2NaHCO_3 \quad (4)$$

$$(R_2NH_2)_2SO_4 + 2Na_2CO_3 + 2H_2O = 2R_2NH_2OH + Na_2SO_4 + 2NaHCO_3 \quad (5)$$

Subsequent recovery of uranium from the aqueous liquors may be achieved by several known methods.

In stripping with strong acids such as hydrochloric or nitric, advantage is taken of the relatively strong affinity of the amine for these acids as compared to that for either sulfuric acid or the uranium sulfate complex. As mentioned previously, the reactions involved may be considered to be essentially the same as those experienced with the weak base anion exchange resins, e.g.,

$$(R_2NH_2)_2UO_2(SO_4)_2 + 2HNO_3 \longrightarrow 2R_2NH_2NO_3 + UO_2^{++} + 2HSO_4^- \quad (6)$$

and

$$(R_2NH_2)_2SO_4 + 2HNO_3 \longrightarrow 2R_2NH_2NO_3 + H_2SO_4 \quad (7)$$

With some exceptions (see below), the amine nitrate and chloride salts remain dissolved in the hydrocarbon solvent and could be recycled to the extraction system in this form. Either salt, however, will be a less effective extractant for uranium than the free amine due to the competition reaction described in Equations (6) and (7).

Each of the stripping agents mentioned above has been examined for its effectiveness in removing uranium from hydrocarbon (Amsco D-95) solutions of several different amines, and the results from these experiments are presented in Table 12. In each test, the organic solution was prepared by prior extraction from a synthetic leach liquor such that the uranium content of the pregnant organic was about 2.5 g U/l. Contact between this solution and the aqueous stripping agents was achieved by shaking vigorously in a separatory funnel for 2-3 minutes. After the phases had been separated, the distribution of uranium was measured in the usual manner. Filtration of both the organic and aqueous layers was necessary in those cases where a uranium precipitate was formed.

The hydroxide stripping method presents the simplest flowsheet and, barring scale-up difficulty, perhaps the best economy in operation and reagent consumption since the uranium product is obtained directly as a natural result of the stripping step. As shown in Table 12, complete removal of uranium may be accomplished by using only a 20% excess of sodium hydroxide over the combined stoichiometric requirements for conversion of the amine salt to free amine (Eq. 2) and precipitation of the uranium as sodium diuranate (Eq. 1). With ammonium hydroxide, a much larger excess (200%) is required although there is some indication that more efficient utilization of this reagent could be achieved by prolonging the contact time. In either case, provided sufficient total reagent were present, the uranium recovery was essentially independent of the initial reagent concentration. In actual practice the choice between dilute and concentrated reagents would probably be made on the basis of difference in operational characteristics. For example, when the hydroxide was added as a very concentrated solution, such a small aqueous volume was required that the resultant system contained only two distinct phases, i.e., the organic solvent plus a wet uranium precipitate. This precipitate settled fairly rapidly from the solvent and appeared to be easily recoverable by filtration or centrifugation, possibly combined with decantation. When dilute bases were used, most of the precipitate was collected at the interface but small

## Table 12

## URANIUM STRIPPING

| Amine[a] | Stripping Agent[b] | Phase Ratio, o/a | U Stripped % | U Stripped $S_a$[c] | Remarks |
|---|---|---|---|---|---|
| Di-n-decyl | Water | 1 | 1.5 | 0.015 | Fast separation |
| | 2% $Na_2CO_3$ | 1 | 99.8 | 600 | " " |
| | 8% " | 4 | 100 | >1000 | " " |
| | " " | 6 | 99.9 | >1000 | " " |
| | " " | 8 | 69 | 20 | " " |
| | 12% " | 6 | 100 | >1000 | " " |
| | " " | 9 | 100 | >1000 | " " |
| | " " | 12 | 78 | 40 | " " |
| | 2% $(NH_4)_2CO_3$ | 1 | 99 | 100 | Fairly fast sepn. |
| | 1% NaOH | 2 | 36 | (d) | " " " (e) |
| | " " | 1 | 100 | (d) | " " " (e) |
| | 2% " | 4 | 30 | (d) | " " " (e) |
| | " " | 2 | 100 | (d) | " " " (e) |
| | 0.1M HCl + 0.9M $NH_4Cl$ | 1 | 99 | 90 | Very slow-breaking emulsion |
| | 1.0M $HNO_3$ | 1 | 99.7 | 350 | Fairly fast sepn. |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 1 | 99.8 | 400 | " " " |
| Dilauryl | 2% $Na_2CO_3$ | 1 | 99.9 | 1000 | Fast sepn. |
| | 5% " | 1 | 100 | >1000 | " " |
| | 10% " | 1 | 100 | >1000 | " " |
| | 10% $(NH_4)_2CO_3$ | 1 | 99.8 | 400 | Fairly slow sepn. |
| | 2% NaOH | 1 | 100 | (d) | Fast sepn. (e) |
| | 2% $NH_3$ Soln. | 1 | 97.9 | (d) | Very slow sepn. (e) |
| | 1.0M HCl | 1 | 99.6 | 250 | Emulsion[f] |
| | 0.1M HCl + 0.9M $NH_4Cl$ | 1 | 99.4 | 170 | Emulsion[f] |
| | 1.0M $HNO_3$ | 1 | 99.8 | 650 | Emulsion[f] |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 1 | 99.8 | 350 | Emulsion[f] |
| | 40% NaOH | 67 | 98.2 | (d) | 19% excess base. Filtered readily.[h] |
| | " " | 67[g] | 99+ | (d) | " " " " " |

Table 12 (Cont'd.)

URANIUM STRIPPING

| Amine[a] | Stripping Agent[b] | Phase Ratio, o/a | U Stripped % | U Stripped $S_o^a$[c] | Remarks |
|---|---|---|---|---|---|
| Dilauryl (Cont'd.) | 40% NaOH | 40 | 99+ | (d) | 100% excess base. Filtered readily.[h] |
| | " " | 40(g) | 99+ | (d) | " " " " " |
| | " " | 25 | 99+ | (d) | 220% " " " " |
| | " " | 25(g) | 99+ | (d) | " " " " " |
| | 16% $NH_3$ Soln. | 67 | 46 | (d) | 18% " " " " |
| | " " " | 67(g) | 47 | (d) | " " " " " |
| | " " " | 40 | 62 | (d) | 95% " " " " |
| | " " " | 40(g) | 80 | (d) | " " " " " |
| | " " " | 25 | 99+ | (d) | 200% " " " " |
| | " " " | 25(g) | 99+ | (d) | " " " " " |
| Methyldi-n-octyl | 2% $Na_2CO_3$ | 1 | 100 | >1000 | Fairly fast sepn. |
| | 2% NaOH | 1 | 99.8 | (d) | " " " (e) |
| | 0.1M HCl + 0.9M $NH_4Cl$ | 1 | 95 | 15 | " " " |
| | 1.0M $HNO_3$ | 1 | 96 | 25 | " " " |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 1 | 95 | 20 | " " " |
| Methyldi-n-decyl | 2% $Na_2CO_3$ | 1 | 100 | >1000 | " " " |
| | 2% NaOH | 1 | 100 | (d) | " " " (e) |
| | 0.1M HCl + 0.9M $NH_4Cl$ | 1 | 90 | 10 | " " " |
| | 1.0M $HNO_3$ | 1 | 95 | 20 | " " " |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 1 | 94 | 15 | " " " |
| Tri-n-octyl | 2% $Na_2CO_3$ | 1 | 99.3 | 150 | " " " |
| | 2% NaOH | 1 | 99.9 | (d) | " " " (e) |
| | 0.1M HCl + 0.9M $NH_4Cl$ | 1 | 92 | 10 | " " " |
| | 1.0M $HNO_3$ | 1 | 97 | 35 | " " " |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 1 | 97 | 30 | " " " |

Table 12 (Cont'd.)

URANIUM STRIPPING

| Amine[a] | Stripping Agent[b] | Phase Ratio, o/a | U Stripped % | U Stripped $S_o^a$[c] | Remarks |
|---|---|---|---|---|---|
| Tri-n-octyl (Cont'd.) | 8% $Na_2CO_3$ | 8[i] | 90 | 70 | Contacted for 5 min at 25°C. |
| | " " | 8 | 95 | 150 | " " " " at 40° |
| | " " | 8 | 98 | 400 | " " 1 hr at 25° |
| | " " | 8 | 98 | 400 | " " " " at 40° |
| | " " | 8 | 99.2 | 1000 | " " 2 hr at 25° |
| | " " | 8 | 99.4 | 1000 | " " " " at 40° |
| | " " | 10[i] | 52 | 10 | " " 5 min at 25° |
| | " " | 10 | 60 | 15 | " " " " at 40° |
| | " " | 10 | 63 | 20 | " " 1 hr at 25° |
| | " " | 10 | 80 | 40 | " " " " at 40° |
| | " " | 10 | 73 | 30 | " " 2 hr at 25° |
| | " " | 10 | 87 | 70 | " " " " at 40° |
| Tri-n-decyl | 1.0M $HNO_3$ | 2 | 91 | 20 | Fairly fast sepn. |
| | 0.1M $HNO_3$ + 0.9M $NH_4NO_3$ | 2 | 92 | 25 | " " " |

(a) The pregnant organic head was a 0.1M solution of the designated amine in Amsco D-95, loaded to ~2.5 g U/l by extraction at $2^a:1^o$ from a synthetic leach liquor containing 1.25 g U/l, 5.3 g Fe/l, 3.5 g Al/l, 0.02M $PO_4$, 0.09M F, 0.5M $SO_4$, pH 0.9.

(b) Stripping conditions: Single-stage contact of pregnant organic head with designated agent at designated phase volume ratio; contact for 2 min. at room temperature except where otherwise noted. (Percent concentrations are weight/volume %.)

(c) Stripping coefficient, $S_o^a$ = (Final U concn. in Aq.)/(Final U concn. in Org.).

Table 12 (Cont'd.)

URANIUM STRIPPING

(d) Uranium stripped in the form of a precipitate.

(e) Precipitate present in both phases, principally near interface. Both phases filtered.

(f) Emulsions broken by filtration; a small amount of precipitated amine salt was present.

(g) Five minutes instead of two minutes contact time.

(h) No apparent aqueous phase: The small amount of aqueous solution was completely absorbed by the uranium precipitate.

(i) 8% Sodium carbonate at $8^{o}:1^{a}$ was equivalent to 70% of theoretical, and at $10^{o}:1^{a}$, 56% of theoretical, based on equations (4) and (5), p. 79.

amounts were also dispersed throughout both the organic and aqueous layers. In this case, separation of the rather slimy hydrolytic precipitate from both the aqueous and organic phases would be necessary and, thus, for a plant scale the operational problems would appear to be somewhat more difficult than the case described above.

In the hydroxide stripping, any iron or other hydrolyzable metal extracted or entrained by the organic phase will be precipitated along with the uranium. For example, in preliminary cyclic extractions from a highly contaminated liquor* with di-n-decylamine, the resulting products contained about 10% $Fe_2O_3$. With the more selective tri-n-octylamine, the products were of higher grade, ordinarily containing less than 2% $Fe_2O_3$. In either case, the extent of contamination should represent about the maximum to be expected in actual process practice. Improvement in product grade could probably be obtained, if desired, either by using a higher aqueous to organic ratio such that most of the iron extracted in the lower stages would be replaced by uranium in the upper stages, or by "scrubbing" the organic with dilute sulfuric acid prior to the stripping step in order to remove both the entrained aqueous liquor and the extracted iron.

In the carbonate method, complete stripping of the uranium was obtained in a single-stage, two-minute contact using about 60% excess sodium carbonate over the requirements shown by Equations 4 and 5. Ammonium carbonate was also an effective reagent although somewhat inferior to sodium carbonate. With sodium carbonate, and presumably also with ammonium carbonate, some savings in reagent can be gained by increasing the time and/or temperature of the stripping operation. Additional savings might be obtained by using multistage rather than single stage contacting. In any case, however, as shown both by the results reported here and the results from other work, the cost of the carbonate strip should not be great. For example, in laboratory process tests using single stage contact, strip solutions containing about 25 g U/l have been obtained at the expense of only 5 lbs of $Na_2CO_3$ per lb of recovered uranium.

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*This was a synthetic liquor simulating a leach liquor obtained from Marysvale ore: 1.25 g U/l, 5.3 g Fe/l, 3.5 g Al/l, 0.02M $PO_4$, 0.09M F, 0.5M $SO_4$, pH 0.9. Much lower concentrations of iron (and also aluminum) would ordinarily be expected in leach liquors from the carnotite sandstone ores.

As pointed out previously, the uranium reacts with the sodium carbonate solution to form a soluble complex rather than a solid precipitate as is the case with sodium hydroxide. Iron, on the other hand, reacts similarly with either reagent, forming a precipitate of ferric hydroxide which collects predominantly at the interface. Thus, the carbonate stripping method effects an additional separation of uranium from iron but at the same time creates a source of potential difficulty in process application. In practice, it would be advisable to keep the extracted iron at a minimum by using the more selective reagents and/or by modifying the extraction cycle according to the methods proposed above. Even with these precautions, clarification of both the organic and aqueous components of the stripping system might be required on an intermittent basis.

The acidic nitrate and chloride solutions are less efficient stripping agents than either of the two types of basic solutions described above. However, if multistage stripping is provided, their performance should be satisfactory and they may be considered as offering still another method for recovering uranium from the pregnant organic solvent with reasonable reagent economy.

From the results in Table 12, it may be observed that the nitrate solutions are much more effective stripping agents than are the chloride solutions, although the latter reagent might be a better choice for process application due to considerations discussed in Section E. In other respects, the performance of the reagents were fairly similar. For example, the response from the secondary amines was better than from the tertiary amines for both reagents and, in either case, the effect of solution pH was small i.e., the coefficients for 1.0M acid solutions were not much higher than those for 1.0M salt solutions at a pH of 1.0. This latter effect, or rather lack of effect, might be of advantage in reducing the cost for reagents in the stripping step. For example, the uranium could be precipitated from the acidic strip solution by neutralization with sodium or ammonium hydroxide, and some of the mother liquor from this operation, modified with a small amount of additional acid, could be recycled to subsequent stripping cycles. The amount of recycle which could be profitably achieved would depend, of course, upon the rate at which sulfate was built up in the liquor, in accordance with Equation (6) or (7).

Physical difficulties were encountered with the nitrate and chloride if the stripping was done at room

temperature and if the extractant was a long normal chain secondary amine such as di-n-decyl- or dilaurylamine. Very slow breaking emulsions were formed in these instances, apparently due to partial precipitation of the amine nitrate or chloride salt. To alleviate this difficulty, it was necessary to perform the stripping operation at temperatures above 35°C. Similar separation troubles were not encountered with the tertiary or the branched-chain secondary amines.

## I. EXTRACTION AND STRIPPING OF VANADIUM

The extraction of vanadium(V) from acidic sulfate solutions was discussed briefly in Section C. Table 13 presents results from additional extractions made at different sulfate levels and with a wider variety of amines. The vanadium head solutions used for these tests were prepared by dissolving sodium metavanadate in dilute sulfuric acid solution and adjusting the sulfate concentration to the desired level with sodium sulfate.

It is demonstrated again by these data that the vanadium(V) extractions are exceedingly dependent upon the acidity of the aqueous solution. At a pH of 1, the extraction coefficients were usually less than one, increasing gradually with an increase of pH to 2.0 and sharply thereafter. With increased concentrations of sulfate in the aqueous, from 0.5 to 1.0M, the extractions in general were decreased, although there were some apparent contradictions to this at the higher pH levels. These apparent inconsistencies may have been due to variations in analytical determinations at the low vanadium level. Tests with ore leach liquors, to be reported later, have served to confirm in general the results with pure solutions described above. As mentioned previously, these tests have also shown that vanadium(IV) is not significantly extracted from sulfate liquors over a pH range from 1 to 2.

Investigations of methods for stripping vanadium from the pregnant organic solutions (0.1M amine in D-95 or benzene) are described by the data in Table 14. Basic solutions of sodium carbonate, sodium hydroxide, or ammonium hydroxide are shown to be effective stripping agents. It may be noted that whereas uranium is precipitated by the latter two reagents, it should be possible to keep the

Table 13

EXTRACTION OF VANADIUM(V) FROM ACIDIC SULFATE SOLUTIONS WITH AMINES

| Amine | Diluent | 0.5M $SO_4$ | | | | | | 1.0M $SO_4$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH* | $E_a^o$ | pH* | $E_a^o$ | pH* | $E_a^o$ | pH* | $E_a^o$ | pH* | $E_a^o$ | pH* | $E_a^o$ |
| C&CCC 21F81 | Benzene | --- | --- | --- | --- | --- | --- | 1.1 | .3 | 1.9 | 1.5 | 4.7 | >30 |
| C&CCC 16F27 | Benzene | --- | --- | --- | --- | --- | --- | 1.1 | 1 | 1.8 | 2 | 2.8 | 25 |
| Di-n-decyl | Amsco D-95 | 1.2 | 1.5 | 1.8 | 5 | 2.6 | 80 | 1.1 | .7 | 1.7 | 2 | 2.4 | 30 |
| " | " | --- | --- | 1.5 | 3 | 2.6 | >40 | --- | --- | 1.4 | .8 | 2.2 | 10 |
| Armeen 2-12 | " | 1.2 | 1.0 | 1.7 | 7 | 2.6 | 15 | 1.1 | 1 | 1.7 | 3 | 2.3 | 25 |
| Armeen 2C | " | 1.1 | .7 | 1.7 | 5 | 2.5 | 50 | 1.1 | 1 | 1.7 | 3 | 2.3 | 7 |
| Methyldi-n-octyl | Benzene | --- | --- | --- | --- | --- | --- | 1.1 | .5 | 1.9 | 3 | 3.0 | 30 |
| " " | Amsco D-95 | 1.1 | .3 | 1.7 | 4 | 2.4 | 20 | 1.1 | .3 | 1.7 | 1.5 | 2.3 | 25 |
| Methyldi-n-decyl | Amsco D-95 | --- | --- | 1.8 | 5 | 2.5 | 45 | 1.1 | .3 | 1.7 | 2 | --- | --- |
| Tri-n-octyl | Amsco D-95 | 1.1 | .9 | 1.7 | 3 | 2.2 | 20 | 1.1 | .7 | 1.6 | 1 | 2.1 | 25 |

0.1M Amine; $2^a:1^o$ phase ratio; 0.8-0.9 g V/l in head solution.

*Equilibrium pH.

Table 14

STRIPPING OF VANADIUM

| Pregnant Amine | Diluent | g V/l in Head Organic | Stripping Agent | Phase Ratio Org./Aq. | Stripping Coefficient, $S_o$[a] |
|---|---|---|---|---|---|
| C&CCC 21F81[1] | Benzene | 0.36 | .1M HCl + .9M $NH_4Cl$ | 2 | 6 |
| " " | " | " | 2% $Na_2CO_3$ | " | > 35 |
| " " | " | " | 5% $Na_2CO_3$ | " | > 35 |
| C&CCC 16F27[1] | " | " | .1M HCl + .9M $NH_4Cl$ | " | > 35 |
| " " | " | " | 2% $Na_2CO_3$ | " | > 35 |
| " " | " | " | 5% $Na_2CO_3$ | " | > 35 |
| Di-n-decyl[2] | Amsco D-95 | 1.6 | .1M HCl + .9M $NH_4Cl$ | 1 | < .1 |
| " " | " | " | .1M $HNO_3$ + .9M $NaNO_3$ | " | .8 |
| " " | " | " | 2% $Na_2CO_3$ | " | > 70 |
| " " | " | " | 8% $Na_2CO_3$ | " | > 70 |
| " " | " | " | 2% NaOH | " | > 70 |
| " " | " | " | 8% NaOH | " | > 60 |
| " " | " | " | 8% $NH_3$ Solution | " | > 70 |
| Methyldi-n-decyl[2] | Amsco D-95 | 1.6 | .1M HCl + .9M $NH_4Cl$ | " | < .1 |
| " " | " | " | .1M $HNO_3$ + .9M $NaNO_3$ | " | < .1 |
| " " | " | " | 2% $Na_2CO_3$ | " | > 70 |
| " " | " | " | 8% $Na_2CO_3$ | " | > 70 |
| " " | " | " | 2% NaOH | " | > 70 |
| " " | " | " | 8% NaOH | " | 80 |
| " " | " | " | 8% $NH_3$ Solution | " | > 60 |

Table 14 (Cont'd.)

STRIPPING OF VANADIUM

| Pregnant Amine | Diluent | g V/l in Head Organic | Stripping Agent | Phase Ratio Org./Aq. | Stripping Coefficient, $S_o^a$ |
|---|---|---|---|---|---|
| Tri-n-octyl[3] | Amsco D-95 | 1.7 | .1M HCl + .9M $NH_4Cl$ | 1 | 0 |
| " " | " | " | .1M $HNO_3$ + .9M $NH_4NO_3$ | " | .2 |
| " " | " | " | 1M $HNO_3$ | " | .4 |
| " " | " | " | 2% $Na_2CO_3$ | " | >150 |
| " " | " | " | 8% $Na_2CO_3$ | " | >150 |
| Tri-n-octyl[4] | " | 1.1 | $H_2SO_4$ - pH 1.0 | " | <.05 |
| " " | " | " | $H_2SO_4$ - pH .75 | " | <.05 |
| " " | " | " | $H_2SO_4$ - pH .50 | " | <.05 |
| " " | " | " | 1M $SO_4$ Soln., pH 1.0 | " | <.05 |
| " " | " | " | " " , pH .75 | " | <.05 |
| " " | " | " | " " , pH .50 | " | <.05 |

Pregnant organic solutions were prepared by contacting a 0.1M solution of the amine with -

1) twice its volume of a 1.0M $SO_4$ solution containing 0.7 g V/l, pH 1.8.
2) " " " " " " " " 0.9 g V/l, pH 2.4.
3) an equal volume of Lukachukai oxidized liquor containing 2.4 g V/l, pH 2.0.
4) twice its volume of a 0.50M $SO_4$ solution containing 1 g V/l, pH 2.2.

vanadium(V) dissolved, for the most part, in the aqueous phase. With chloride solutions (0.1M HCl - 0.9M $NH_4Cl$) as the stripping agent, variable results were obtained. In two instances, shown in Table 14, the stripping was almost complete; in all other tests, the coefficients (a/o) were less than 0.1. The mode of occurrence of vanadium in the organic phase was apparently different in these tests due to differences in the solvent, the amine, possibly the loading level, and possibly also the conditions, i.e., pH, at which the vanadium was originally extracted (see footnote, Table 14). Similarly, a change in the chemical form of the vanadium after extraction is suggested by the failure to strip vanadium with 1M sulfate solution at pH 1 (or even 0.5), although vanadium extraction from such a solution was low. Further studies in this system are being made.

Although the information on extraction and stripping of vanadium as reported above is somewhat limited, it is generally apparent that the amines may be chemically suitable for the separate recovery of both uranium and vanadium from sulfate liquors in which these elements coexist. Preferential extraction of uranium may be obtained at the lower pH levels if the vanadium is oxidized, and in any case if the vanadium is reduced; subsequent extraction of vanadium could be obtained after pH adjustment and/or oxidation of the leach liquor. Co-extraction of uranium and vanadium would also be possible at the higher pH levels. In such a case, the separation of vanadium from uranium would be accomplished either as a part of the stripping cycle or in a separate, subsequent operation.

Continued process development studies of the uranium-vanadium liquors are being made and will be described in a later report. The following aspects will be of particular interest: (1) the effect of iron on the extraction at higher pH levels with the less selective amines, (2) the identification of those amines which can be used at a sufficient concentration in various organic solvents for the simultaneous extraction of both uranium and vanadium to be achieved, (3) the extent of the separation of uranium and vanadium that can be obtained by various stripping methods, (4) reagent costs, and (5) determination of the optimum combination of operating variables.

## J. EXTRACTION OF URANIUM FROM PHOSPHATE, NITRATE, AND CHLORIDE SOLUTIONS

Extraction of uranium from aqueous solutions of phosphoric, nitric, and hydrochloric acids is shown in Table 15. In these tests, the initial uranium concentration was about 1 g/l; the amine used was methyldi-n-decylamine, 0.1M, in benzene solution. The results were qualitatively similar to results obtained in uranium sorption by anion exchange resin from similar acid solutions (cf. Figure 16, Y-816).[7] At low concentration, below 1M, phosphoric acid was favorable for the extraction of uranium, but as the concentration was increased the extraction fell rapidly. This may have been due both to increased competition for the amine by the excess phosphate and to interference (by the increased hydrogen ion concentration) with the formation of favorable uranium complexes.

Very low uranium extraction was obtained from solutions of nitric and hydrochloric acids at low concentrations, as is to be expected from the effectiveness of such solutions (e.g., 1M) in stripping uranium from the loaded organic phase (Section H). However, the amount of uranium extracted increased as the concentration of either acid was increased, presumably because of increasing formation of favorable uranium complexes. Effective extraction was obtained from hydrochloric acid when its concentration was 4M or greater, but the extraction from nitric acid at 4M was still low.

The extraction tests from nitrate were extended to higher concentrations and higher pH, as shown in Table 16. Although these tests are not directly comparable with those in Table 15, as a different reagent (tri-n-octylamine) and somewhat different extraction conditions were used, the results show a small but definite increase of extraction with rise of pH. Practicable extraction coefficients were obtained only at the highest nitrate concentrations tested. Here again, the very low extractions obtained at 1M, pH either 1 or 0.1, conform to the effectiveness of these solutions for stripping uranium from the amines.

Table 15

EXTRACTION OF URANIUM FROM ACIDS

| Initial Acid Concn. M | Initial pH | Final pH | Uranium Extraction Coeff., $E_a^o$ |
|---|---|---|---|
| | Phosphoric Acid | | |
| 0.7 | --- | 1.0 | 15 |
| 1.3 | 0.6 | 0.7 | 2 |
| 2.5 | 0.3 | 0.3 | 0.02 |
| 4.2 | ~0 | ~0 | < 0.01 |
| 6.0 | | | < 0.01 |
| 8.4 | | | < 0.01 |
| | Nitric Acid | | |
| 0.1 | 1.0 | 2.6 | < 0.01 |
| 0.5 | 0.3 | 0.4 | 0.01 |
| 1.0 | ~0 | ~0 | 0.03 |
| 1.9 | | | 0.10 |
| 2.6 | | | 0.14 |
| 4.6 | | | 0.26 |
| | Hydrochloric Acid | | |
| 0.1 | --- | 1.6 | < 0.01 |
| 0.7 | 0.3 | 0.4 | 0.04 |
| 1.4 | ~0 | ~0 | 0.2 |
| 3.8 | | | 7 |
| 6.0 | | | 90 |
| 8.8 | | | 500 |

Extraction Conditions:

Initial aqueous uranium concentration, 1 g/l ≈ 0.004M.
Organic phase, 0.1M methyldi-n-decylamine in benzene.
Phase ratio, 1:1.

Table 16

EXTRACTION OF URANIUM FROM NITRATE SOLUTIONS

| Initial Nitrate Concn. M | Initial pH | Final pH | Uranium Extraction Coeff., $E_a^o$ |
|---|---|---|---|
| 1.0 | 0.1 | 0.1 | 0.03 |
| 2.0 | " | " | 0.1 |
| 2.8 | " | " | 0.3 |
| 3.6 | " | " | 0.7 |
| 4.5 | " | " | 1.5 |
| 5.5 | " | " | 3. |
| 1.1 | 0.9 | 0.9 | 0.06 |
| 2.1 | " | 0.8 | 0.2 |
| 3.1 | " | 0.9 | 0.8 |
| 4.0 | " | 1.0 | 1.5 |
| 5.0 | " | 1.0 | 3. |
| 6.0 | " | 0.9 | 7. |

Extraction Conditions:

Initial aqueous uranium concentration, 1.25 g/l $\approx$ 0.005M.
Organic phase, 0.1M tri-n-octylamine in Amsco D-95.
Phase ratio, 2 aqueous : 1 organic.

## IV. SUMMARY

Over 100 different organonitrogen compounds have been examined for their ability to extract uranium from aqueous solutions, particularly sulfate solutions, of the types usually encountered in uranium ore processing. The more promising of these have been examined further with respect to other characteristics essential to practical application, especially selectivity for uranium, reagent loss to the aqueous phase, compatibility with practicable diluents, maintenance of adequate extraction power over a range of liquor compositions, and compatibility with practicable stripping methods. The principal conclusions to be drawn from the tests may be listed as follows:

1. A number of long-chain aliphatic primary, secondary, and tertiary amines in organic diluents have been shown to be remarkably effective extractants for uranium from acidic sulfate liquors. Some of the more promising of these were

Tri-n-octylamine (Tertiary)
Tri-n-decylamine "
Trilaurylamine "
Di-n-hexyllaurylamine "
Methyldi-n-decylamine "
Dilaurylamine (Secondary)
Di-n-decylamine "
"C&CCC 16F27" (a branched-chain secondary amine with 24 carbon atoms)
"Primene JMT" (a 1,1-dimethylalkyl- primary amine with about 20 carbon atoms)
"C&CCC 21F81" (a branched-chain primary amine with 17 carbon atoms)

Little or no extraction power was shown by compounds from several other organonitrogen classes, including some polyamines and quaternary ammonium salts. However, the compounds which were available were not necessarily of optimum molecular weight, etc., for use in solvent extraction, and the classes represented need not be considered eliminated from future investigation.

2. The tertiary, especially the symmetrical tertiary, amines have shown a remarkable preference for uranium over the other elements frequently found in ore leach liquors. The secondary amines, although less selective than the tertiaries, have also been good in this respect. With

either type of amine, molybdenum, which infrequently appears at appreciable concentrations in the liquors, is the only element of those tested which offered any major selectivity problem. In special cases, it would probably be necessary to separate uranium and molybdenum either in the stripping cycle or in a subsequent operation. The primary amines, in contrast to the secondaries and tertiaries, have shown very poor selectivity particularly in regard to ferric iron and, on this basis, have been deferred from further immediate consideration. They do not, however, extract ferrous iron and, thus, might find application if the iron in the liquors were reduced. Attention will be given later to this possibility.

3. The amount of reagent lost in the extraction process by dissolution in (distribution to) the aqueous phase is dependent primarily upon the particular reagent and solvent used and, to a lesser extent, upon the acidity and salt concentration of the aqueous solution. When the alkyl chains are sufficiently long, only insignificant quantities of the amines are distributed to liquors of the composition ordinarily encountered in raw material processing. In actual practice, a more important source of reagent loss would arise through physical entrainment of the organic solution in the aqueous phase.

4. For process purposes, the solvents showing greatest compatibility with the different amines were petroleum products of the high aromatic type, e.g., Amsco D-95, Amsco G, Solvesso 100, Solvesso 150, etc., with Amsco D-95 being the best of this group. Some of the amines could apparently be used in mixtures of these solvents with kerosene whereas certain others, e.g., tri-n-decylamine, might be used under favorable conditions with kerosene alone. From the standpoint of extraction performance only, solvents such as benzene and carbon tetrachloride were superior to those mentioned. These materials would not be acceptable for process purposes, however, due to factors such as high cost, low flash point, and appreciable solubility in the aqueous phase.

5. With the better amine-diluent mixtures, the rates of phase disengagement have been quite rapid from a fairly wide variety of aqueous liquors. In instances wherein the rates were slow, they could be speeded, and usually brought into the range of commercial application, by adding either a suitable surface active agent or a long chain alcohol to the system, or by increasing the extraction temperature. Further studies of the phase separation variables, under conditions which closer simulate those expected in plant practice, must be made on a larger scale.

6. The extraction coefficients for uranium from sulfate solutions at pH ~1 were found to be directly proportional to the concentration of amine in the organic phase. This relationship, together with others involving the amine concentration, suggests that the amines tested exist in the hydrocarbon diluents in a form (such as a colloidal dispersion) in which the amine activity is constant over a wide range of nominal concentrations.

7. The extraction coefficients for uranium from sulfate solutions were found to be sensitive to temperature, pH, sulfate level and to the concentration of other anions in the aqueous phase. Over the range of conditions usually encountered in ore leach liquors, the extractions have been satisfactory, however, if concentration of amine in the organic diluent was only 0.1 molar. When the aqueous uranium concentration was in the order of 1 g/l, the loading of the amine phase was fairly constant at approximately one mole of uranium per 5-6 moles of amine. With amine concentrations at 0.1M, this would correspond to about 4 g of uranium per liter in the pregnant organic phase.

8. Effective stripping of uranium from the amine-diluent mixtures may be obtained with several types of reagents, as for example, dilute acidic chloride solutions, sodium carbonate solutions, and solutions of sodium or ammonium hydroxide. In the latter case, the uranium is directly precipitated from the organic phase. The reagent costs would be somewhat different for the various methods but they should not in any case be high. Differences in operational characteristics would probably be equally important in choosing the method best suited for a particular application.

9. Preliminary studies indicate that the amines may be chemically suitable for the recovery of both uranium and vanadium from sulfate liquors in which these elements coexist. Either separate or simultaneous extractions can be achieved by appropriate adjustment of the extraction conditions; separation of vanadium from uranium in the latter case would be accomplished either during or subsequent to the stripping operations. Further studies of these methods are being made to establish optimum conditions and to determine their economic feasibility.

In general summary of the work with the organonitrogen compounds, it may be observed that most of the compounds originally considered have been found worthy of only cursory examination. The important outcome on the other hand is that several compounds, specifically the long chain

secondary and tertiary amines of the type listed under (1) above, have been identified as having considerable promise for practicable solvent extraction application. In the tests thus far, the best and most versatile performance has been given by the symmetrical tertiary amines. In some ways, particularly in regard to diluent limitations, the least versatile performance has been given by the straight-chain secondary amines, whereas the general performance of the branched secondary amines and the unsymmetrical tertiary amines seems to be intermediate.

Several of these types of reagents have already been examined in laboratory process tests, under simulated plant conditions, and the results so far from this work have been favorable. Semipilot plant tests are now being planned in order to obtain better data concerning reagent entrainment, phase separation, and other operational factors which are important in defining the processing costs, but which cannot be adequately studied on a laboratory scale.

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The preliminary test results pertaining to the mechanism of extraction were contributed by Dr. C. F. Baes.

Most of the analyses were performed by the Y-12 Section of the ORNL Analytical Division under the direction of Mr. C. D. Susano.

Many of the reagents which were obtained from outside sources were furnished as product samples by the manufacturers. In addition, special reagents were contributed by the research laboratories of Armour Chemical and Research Divisions of Armour and Company, and of Carbide and Carbon Chemicals Company.

## VI. REFERENCES


1. "Progress Reports, Uranium Chemistry of Raw Materials Section, July 1, 1951 to September 30, 1952," ORNL - Y-12, Y-823, ORNL-1220, ORNL-1308, ORNL-1384, ORNL-1480.

2. E. Lester Smith and J. E. Page, "The Acid-Binding Properties of the Long Chain Aliphatic Amines," Journal of the Society of Chemical Industry (London), 67, 48-51 (Feb., 1948).

3. G. W. Leddicotte and F. L. Moore, "A New Solvent Extraction Method for the Separation of Niobium and Tantalum," J. Am. Chem. Soc., 74, 1618 (March, 1952).

   F. L. Moore, "A New Anionic Solvent Extraction Technique," ORNL, ORNL-1314, July 3, 1952.

4. "Progress Report for September 16, 1951 - November 15, 1951," American Cyanamid Company, ACCO-15, pp. 46 ff.

   Sallie A. Fisher, "Investigation of Ion Exchange Resins in Use at West Rand," Rohm & Haas Company, RMO-2521, April, 1953; RMO-2524, June, 1953.

5. Al Preuss, "The Prevention of Cobalticyanide Poisoning of Ion Exchange Resins used on South African Gold Ore Residue Leach Liquors," Rohm & Haas Company, RMO-2523, June, 1953.

6. James S. Fritz, Acid-Base Titrations in Nonaqueous Solvents, The G. Frederick Smith Chemical Company, Columbus, Ohio, 1952.

   Pifer, C. E., and E. G. Wollish, "Potentiometric Titrations of Salts of Organic Bases in Acetic Acid," Anal. Chem., 24, 300 (1952).

7. Spivey, E. V., E. L. Leyshon, F. J. Hurst, D. J. Crouse, and C. F. Coleman, "Topical Report on Anion Exchange Studies," ORNL - Y-12, Y-816, October, 1951.

8. Saine, V. L., and K. B. Brown, "Studies of Recovery Processes for Western Uranium-Bearing Ores," C&CCC - Y-12, AECD-3241, October 14, 1949.

# APPENDIX A

## PURITY OF COMPOUNDS

R. S. Lowrie

The organonitrogen compounds from Armour were prepared from coconut oil, animal tallows and soybean oil. The starting materials were converted first to the nitrile followed by catalytic hydrogenation to form the amines, which were used, in turn, as starting materials in the preparation of quaternary ammonium compounds and polyamines. According to descriptive literature from the manufacturer, the purity levels of the amines (Armeens) were about 80-90%. The quaternary ammonium salts (Arquads) and polyamines (Duomeens) were ordinarily described as containing 75-80% active material. The impurities in these reagents were probably mostly homologous compounds derived from the homologous impurities present in the starting materials, together with mixtures of the amine classes (e.g., contamination of a secondary amine with the corresponding primary and tertiary amines). Other materials, such as polyamines, unreacted starting materials or intermediates, and hydrocarbons, would be expected to be present in smaller quantities.

The compounds obtained from Eastman Kodak were of Eastman Grade (white label) whenever possible. Their purity can best be indicated by this statement from the current listing (No. 38) of Eastman Organic Chemicals:

> Eastman Grade: These are the highest purity chemicals and are suitable for reagent use or for the more exacting syntheses. They are essentially free from isomers, homologs and impurities and can be used for all chemical applications except physical chemical measurements.

The majority of compounds obtained from Carbide and Carbon Chemicals Company were laboratory samples, made from aldehydes produced in synthetic organic chemical processes such as the "OXO" process. Descriptive information as to the purity level of these compounds was not furnished, but a comparison at this laboratory of the experimentally determined equivalent weights with the theoretical equivalent weights showed 90-95% agreement in most cases. The method used for these comparisons (nonaqueous titration) gave only the average equivalent weight and did not distinguish among the various compounds present. The most

likely impurities, however, are alcohols, water, other amines and possibly unreacted starting materials.

The amines from specialty houses and other commercial sources ordinarily showed 80-90% agreement between the theoretical and experimentally determined equivalent weights. Again, the most likely impurities present are unreacted starting materials, water and other amines, some of which at least are of a lower molecular weight as shown by solubility measurements.

By using relatively pure starting materials and careful separation of products by distillation, the purity levels of compounds prepared at ORNL were ordinarily better than 90%, based on equivalent weight determinations and carbon-hydrogen-nitrogen analyses. A brief description of the methods used in preparing these compounds may be found in Appendix B.

## DESCRIPTION OF COMPOUNDS

### Primary Amines

| Amine | Source[d] | Formula | Description[b] | Mol. Wt.[a] Theo. | App. |
|---|---|---|---|---|---|
| 3,5,5-Trimethylhexyl | EK | $(CH_3)_3CCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2NH_2$ | Eastman Grade "White Label" | 143 | |
| Armeen 10D | Ar | $CH_3(CH_2)_9NH_2$ | 90% Decyl, 3% octyl, and 7% lauryl | 157 | |
| Armeen 12D | Ar | $CH_3(CH_2)_{11}NH_2$ | 90% Lauryl, 9% tetradecyl | 185 | |
| Armeen CD | Ar | $R\text{-}NH_2$, straight-chain alkyls from coconut oil. | 47% Lauryl, 18% tetradecyl, 8% hexadecyl, 5% octadecyl, 8% octyl, 9% decyl, 5% octadecenyl | 200 | |
| Armeen 14D | Ar | $CH_3(CH_2)_{13}NH_2$ | 90% Tetradecyl, 4% lauryl and 4% hexadecyl | 213 | |
| Armeen 14D (redistilled) | OR | $CH_3(CH_2)_{13}NH_2$ | Analysis - C 79.85, H 14.5, N 6.15%<br>Theo. - C 78.79, H 14.6, N 6.56% | 213 | 231 |
| Armeen 16D | Ar | $CH_3(CH_2)_{15}NH_2$ | 90% Hexadecyl, 6% octadecyl and 4% octadecenyl | 244 | |
| Armeen 16D (redistilled) | OR | $CH_3(CH_2)_{15}NH_2$ | Analysis - C 80.20, H 14.44, N 5.59%<br>Theo. - C 79.59, H 14.61, N 5.80% | 241 | 247 |
| Armeen TD | Ar | $R\text{-}NH_2$, straight-chain alkyls from tallow. | 30% Hexadecyl, 25% octadecyl and 45% octadecenyl | 263 | |
| Armeen HTD | Ar | $R\text{-}NH_2$, straight-chain alkyls from hydrogenated tallow. | 25% Hexadecyl, 70% octadecyl and 5% octadecenyl | 264 | |
| Armeen SD | Ar | $R\text{-}NH_2$, straight-chain alkyls from soy bean oil. | 10% Hexadecyl, 10% octadecyl, 35% octadecenyl and 45% octadecadienyl | 266 | |
| Armeen 18D | Ar | $CH_3(CH_2)_{17}NH_2$ | 93% Octadecyl, 6% hexadecyl and 1% octadecenyl | 267 | |
| Cyclohexylmethyl | C | $\overline{CH_2(CH_2)_4CH}\ CH_2NH_2$ | | 113 | 121 |
| 21F75 | C | (c) | Laboratory sample of a branched-chain aliphatic 11 carbon primary amine | 171 | 182 |
| 18F65 | C | (c) | Laboratory sample of a branched-chain aliphatic 12 carbon primary amine | 185 | 231 |
| 21F79 | C | (c) | Laboratory sample of a branched-chain aliphatic 14 carbon primary amine | 213 | 232 |
| 21F81 | C | (c) | Laboratory sample of a branched-chain aliphatic 17 carbon primary amine | 255 | 271 |
| Primene 81T | RH | $R\text{-}\underset{\displaystyle (CH_3)_2}{\underset{|}{C}}\text{-}NH_2$ R is a highly branched 9-12 carbon alkyl. | 96% Amine, 4% inert | 185 to 227 | 217[a] |
| Primene JMT | RH | $R\text{-}\underset{\displaystyle (CH_3)_2}{\underset{|}{C}}\text{-}NH_2$ R is a highly branched 15-21 carbon alkyl. | 87-89% Amine, 11-13% inert | 270 to 354 | 341[a] |

### Secondary Amines

| | | | | | |
|---|---|---|---|---|---|
| Methyllauryl | Ar | $CH_3\text{-}NH\text{-}(CH_2)_{11}CH_3$ | Laboratory sample | 199 | |
| Di-n-heptyl | EK | $[CH_3(CH_2)_6]_2NH$ | Eastman Grade "White Label" | 213 | |
| Di-n-octyl (Batch A) | OR | $[CH_3(CH_2)_7]_2NH$ | Analysis - C 79.56, H 14.58, N 5.02%<br>Theo. - C 79.68, H 14.51, N 5.81% | 241 | 249 |
| Armeen 2-8 (Batch A) | Ar | $[CH_3(CH_2)_7]_2NH$ | 85% Secondary, 3% primary, 12% inert materials | 241 | |
| Di-n-decyl (Batch L-65) | OR | $[CH_3(CH_2)_9]_2NH$ | Analysis - C 78.08, H 13.11, N 4.03%<br>Theo. - C 80.72, H 14.57, N 4.70% | 298 | |
| (Batch A) | OR | | ----- | 298 | |
| (Batch B) | OR | | Analysis - C 81.46, H 14.66, N 5.03% | 298 | 298 |
| (Batch C) | OR | | Analysis - C 80.54, H 14.56, N 4.49% | 298 | 295 |
| (Batch D) | OR | | ----- | 298 | 312 |
| (Batch E) | OR | | ----- | 298 | 287 |
| (Batch F) | OR | | ----- | 298 | 309 |
| Dilauryl (Batch A) | OR | $[CH_3(CH_2)_{11}]_2NH$ | Analysis - C 83.2, H 14.2 , N 3.10%<br>Theo. - C 81.5, H 14.54, N 3.96% | 354 | 370 |
| (Batch B) | OR | | ----- | 354 | |
| (Batch C) | OR | | ----- | 354 | 383 |
| Armeen 2-12 | Ar | $[CH_3(CH_2)_{11}]_2NH$ | 85% Secondary, 3% primary, 12% inert | 354 | 378 |
| Di-n-tetradecyl (Batch L-82) | OR | $[CH_3(CH_2)_{13}]_2NH$ | Analysis - C 82.94, H 14.22, N 3.29<br>Theo. - C 82.07, H 14.51, N 3.42 | 410 | |

DESCRIPTION OF COMPOUNDS

Secondary Amines (Cont'd.)

| Amine | Source[d] | Formula | Description[b] | Mol. Wt.[a] Theo. | App. |
|---|---|---|---|---|---|
| Di-n-hexacecyl (Batch L-78) | OR | $[CH_3(CH_2)_{15}]_2NH$ | Analysis - C 82.40, H 14.47, N 3.34%<br>Theo. - C 82.51, H 14.50, N 3.00% | 466 | |
| Di-n-octacecyl (Batch L-81) | OR | $[CH_3(CH_2)_{17}]_2NH$ | Analysis - C 82.91, H 14.41, N 2.60%<br>Theo. - C 82.83, H 14.48, N 2.68% | 522 | |
| Armeen 2C | Ar | $R_2NH$, straight-chain alkyls from coconut oil. | 90% Amines, 10% inert | 386 | |
| Armeen 2HT | Ar | $R_2NH$, straight-chain alkyls from hydrogenated tallow. | 90% Amines, 10% inert | 511 | |
| Dicyclohexyl | M | $(CH_2(CH_2)_4CH)_2NH$ | Commercial grade | 181 | |
| 25F25 | C | (c) | Laboratory sample of an alicyclic 16 carbon secondary amine | 237 | 255 |
| 17F22 | C | (c) | Laboratory sample of an alicyclic 18 carbon secondary amine | 264 | 292 |
| Di(2-ethylhexyl) | C | $(C_4H_9-CHCH_2)_2NH$ <br> $C_2H_5$ | | 241 | 247 |
| 2-Ethylhexyl-2-pentylnonyl | OR | $C_4H_9-CHCH_2NHCH_2CH(CH_2)_6CH_3$ <br> $C_2H_5 \quad (CH_2)_4CH_3$ | Analysis - C 82.30, H 14.12, N 4.35%<br>Theo. - C 81.15, H 14.55, N 4.30% | 326 | 326 |
| 15F53 (Batch A) | C | (c) | Laboratory sample of a branched aliphatic 18 carbon secondary amine | 270 | 293 |
| 19F27 | C | (c) | Laboratory sample of a branched aliphatic 24 carbon secondary amine | 354 | |
| Tetradecyl(3-phenylpropyl) | OR | $CH_3(CH_2)_{13}NH(CH_2)_3(C_6H_5)$ | Analysis - C 84.1 , H 12.27, N 3.86%<br>Theo. - C 83.31, H 12.46, N 4.22% | 332 | 319 |
| N-(2-ethylhexyl)-α-methylbenzyl | C | $C_4H_9-CHCH_2NHCH(C_6H_5)$ <br> $C_2H_5 \quad CH_3$ | Laboratory sample | 233 | |
| N-(2-ethylhexyl)-α-xylylbenzyl | C | $C_4H_9-CHCH_2NHCH(C_6H_5)$ <br> $C_2H_5 \quad (C_6H_3)(CH_3)_2$ | Laboratory sample | 324 | 341 |
| n-Butylaniline | EK | $C_6H_5NH(CH_2)_3CH_3$ | Eastman Grade "White Label" | 149 | |
| p,p'-Dioctyldiphenyl | G | $[CH_3(CH_2)_7(C_6H_4)]_2NH$ | | 394 | |
| Dibenzyl | EK | $[(C_6H_5)CH_2]_2NH$ | Eastman Grade "White Label" | 197 | |

Tertiary Amines

| | | | | | |
|---|---|---|---|---|---|
| N,N-dimethyl(2-ethylhexyl) | C | $(CH_3)_2NCH_2CH-C_4H_9$ <br> $C_2H_5$ | Laboratory sample | 157 | |
| Primene 81T - dimethyl | OR | $R-C-N(CH_3)_2$ <br> $(CH_3)_2$ | Methylation product of Primene 81T (q.v.) | | |
| Dimethyl-n-octadecyl | EK | $(CH_3)_2N(CH_2)_{17}CH_3$ | Technical grade | 298 | |
| Dimethyllauryl (Batch A) | EK | $(CH_3)_2N(CH_2)_{11}CH_3$ | Practical grade | 213 | |
| (Batch B) | Ar | | Laboratory sample | 213 | |
| Diethyllauryl | EK | $(C_2H_5)_2N(CH_2)_{11}CH_3$ | Eastman Grade "White Label" | 241 | |
| Bis(β-hydroxyethyl)lauryl | Ar | $CH_3(CH_2)_{11}N(CH_2CH_2OH)_2$ | Laboratory sample | 273 | |
| Dibutyllauryl (Batch A) | OR | $[CH_3(CH_2)_3]_2N(CH_2)_{11}CH_3$ | Analysis - C 81.04, H 14.48, N 4.60%<br>Theo. - C 80.81, H 14.48, N 4.71% | 298 | 292 |
| Dihexyllauryl (Batch A) | OR | $[CH_3(CH_2)_5]_2N(CH_2)_{11}CH_3$ | | 354 | 347 |
| Di(2-ethylhexyl)lauryl (Batch A) | OR | $CH_3(CH_2)_{11}N(CH_2CH-C_4H_9)_2$ <br> $C_2H_5$ | Analysis - C 82.37, H 14.54, N 3.45%<br>Theo. - C 82.16, H 14.41, N 3.42% | 410 | |
| Methyldi-n-octyl (Batch A) | E | $[CH_3(CH_2)_7]_2NCH_3$ | Redistilled at ORNL | 255 | 306 |
| N-methyldi(2-ethylhexyl) (Batch A) | C | $CH_3N(CH_2CH-C_4H_9)_2$ <br> $C_2H_5$ | Laboratory sample | 255 | |
| (Batch B) | C | | Laboratory sample | 255 | 267 |
| Methyldi-n-decyl (Batch A) | OR | $CH_3N[(CH_2)_9CH_3]_2$ | | 312 | |
| (Batch B) | OR | | Analysis - C 82.14, H 13.74, N 4.30%<br>Theo. - C 80.94, H 14.56, N 4.50% | 312 | 308 |
| (Batch C) | OR | | ----- | 312 | |
| (Batch D) | OR | | Analysis - C 81.05, H 14.29, N 4.22% | 312 | 325 |
| (Batch E) | OR | | Analysis - C 81.69, H 14.50, N 4.28% | 312 | 320 |
| (Batch X) | OR | | Analysis - C 80.98, H 14.45, N 4.42% | 312 | 327 |

DESCRIPTION OF COMPOUNDS

Tertiary Amines (Cont'd.)

| Amine | Source[d] | Formula | Description[b] | Mol. Wt.[a] Theo. | App. |
|---|---|---|---|---|---|
| Methyldilauryl (Batch A) | OR | $CH_3N[(CH_2)_{11}CH_3]_2$ | Analysis - C 82.75, H 14.70, N 2.78%<br>Theo. - C 81.66, H 14.52, N 3.81% | 368 | |
| (Batch B) | OR | | Analysis - C 82.46, H 14.67, N 3.72% | 368 | 373 |
| β-Hydroxyethyldilauryl | Ar | $[CH_3(CH_2)_{11}]_2NCH_2CH_2OH$ | Laboratory sample | 398 | |
| Methyldi-n-octadecyl | Ar | $CH_3N[(CH_2)_{17}CH_3]_2$ | Laboratory sample | 536 | |
| Propyldi-n-decyl (Batch A) | OR | $CH_3CH_2CH_2N[(CH_2)_9CH_3]_2$ | | 340 | 336 |
| Tri-n-butyl | Sh | $[CH_3(CH_2)_3-]_3N$ | | 185 | |
| Tri-n-hexyl | ADM | $[CH_3(CH_2)_5-]_3N$ | | 270 | 296 |
| Tri-n-octyl (Batch A) | OR | $[CH_3(CH_2)_7-]_3N$ | Analysis - C 81.77, H 14.16, N 3.47%<br>Theo. - C 81.50, H 14.54, N 3.95% | 354 | 347 |
| (Batch B) | OR | | Analysis - C 82.3 , H 14.2 , N 3.4% | 354 | 310 |
| (Batch C) | OR | | Analysis - C 82.77, H 14.38, N 3.58% | 354 | 390 |
| (Batch D) | OR | | Analysis - C 80.49, H 14.22, N 5.48% | 354 | 372 |
| (Batch E) | OR | | Analysis - C 82.51, H 14.97, N 4.17% | 354 | 379 |
| (Batch G) | B | | ----- | 354 | 402 |
| Tri(2-ethylhexyl) | OR | $(C_4H_9-CHCH_2)_3N$ (with $C_2H_5$) | Analysis - C 82.04, H 14.54, N 3.99%<br>Theo. - C 81.50, H 14.54, N 3.96% | 354 | 347 |
| Tri-n-decyl (Batch A) | OR | $[CH_3(CH_2)_9-]_3N$ | Analysis - C 82.69, H 14.01, N 3.11%<br>Theo. - C 82.29, H 14.50, N 3.20% | 438 | 444 |
| (Batch B) | OR | | Analysis - C 81.95, H 14.40, N 3.64% | 438 | 442 |
| (Batch D) | B | | ----- | 438 | 477 |
| Trilauryl (Batch A) | OR | $[CH_3(CH_2)_{11}-]_3N$ | Analysis - C 79.33, H 14.59, N 3.94%<br>Theo. - C 82.83, H 14.5 , N 2.68% | 522 | 557 |
| (Batch A-1) | OR | | Redistilled Batch A;<br>Analysis - C 82.34, H 14.23, N 2.60% | 522 | 541 |
| N,N-dimethylbenzyl | EK | $(CH_3)_2NCH_2(C_6H_5)$ | Eastman Grade "White Label" | 135 | |
| Tribenzyl | EK | $[(C_6H_5)CH_2]_3N$ | Eastman Grade "White Label" | 288 | |
| N,N-diethylnaphthyl | EK | $(C_2H_5)_2N(C_{10}H_7)$ | Eastman Grade "White Label" | 199 | |
| Di-n-butylaniline | EK | $[CH_3(CH_2)_3]_2N(C_6H_5)$ | Eastman Grade "White Label" | 205 | |
| Ethylbenzylaniline | HD | $(C_6H_5)NCH_2(C_6H_5)$ (with $C_2H_5$) | | 211 | |
| Ethomeen S-15 | Ar | $R-N[(CH_2CH_2O)_5H]_2$, straight-chain alkyls from soy bean oil. | | 494 | |
| Ethomeen S-60 | Ar | $R-N[(CH_2CH_2O)_{50}H]_2$, straight-chain alkyls from soy bean oil. | | 2474 | |
| Ethomeen C-15 | Ar | $R-N[(CH_2CH_2O)_5H]_2$, straight-chain alkyls from coconut oil. | | 426 | |

Quaternary Ammonium Compounds

| | | | | |
|---|---|---|---|---|
| Arquad 2C | Ar | $[(R)_2-N(CH_3)_2]Cl$, straight-chain alkyls from coconut oil. | 73-77% active, 23-27% propanol-2, 1% NaCl. R = 8% octyl, 9% decyl, 47% lauryl, 18% tetradecyl, 8% hexadecyl and 10% octadecyl. | 360 |
| Arquad 2HT | Ar | $[(R)_2-N(CH_3)_2]Cl$, straight-chain alkyls from hydrogenated tallow. | 75% active, 24% propanol-2, 1% NaCl. R = 30% hexadecyl and 70% octadecyl. | 353 |
| Arquad S | Ar | $[R-N(CH_3)_3]Cl$, straight-chain alkyls from soy bean oil | 50% active, 49% propanol-2, 1% NaCl. R = 10% hexadecyl, 10% octadecyl, 35% octadecenyl, 45% octadecadienyl. | 306 |
| Laurylpyridinium chloride | ADM | $[\overline{CH:CHCH:CHCH:N}-(CH_2)_{11}CH_3]Cl$ | | 283 |
| Roccal | S | $[R-N-CH_2(C_6H_5)]Cl$, R = $C_6$ to $C_{12}$ ($CH_3$)$_2$ | 50% Active, 50% $H_2O$. | 318 |
| Cetylpyridinium chloride | ADM | $[\overline{CH:CHCH:CHCH:N}-(CH_2)_{15}CH_3]Cl$ | | 339 |
| Cetyltrimethylammonium bromide | ADM | $[(CH_3)_3N(CH_2)_{15}CH_3]Br$ | | 364 |
| Quaternary C | A | $[CH_3(CH_2)_{10}-\overset{R}{C}:\overline{NCH_2CH_2NR}]Cl$ | | 370 |

## DESCRIPTION OF COMPOUNDS

### Quaternary Ammonium Compounds (Cont'd.)

| Amine | Source[d] | Formula | Description[b] | Mol. Wt.[a] Theo. | App. |
|---|---|---|---|---|---|
| Cetyldimethylbenzyl-ammonium chloride | ADM | $\left[CH_3(CH_2)_{15}\text{-}\underset{(CH_3)_2}{N}\text{-}CH_2(C_6H_5)\right]Cl$ | | 396 | |
| Hyamine 1622 | RH | $\left[(C_6H_5)CH_2\underset{(CH_3)_2}{N}(CH_2CH_2O)_2(C_6H_4)\underset{(CH_3)_2}{C}CH_2C(CH_3)_3\right]Cl.H_2O$ | Pure monohydrate salt | 466 | |
| Hyamine 10X | RH | $\left[(C_6H_5)CH_2\underset{(CH_3)_2}{N}(CH_2CH_2O)_2(\underset{CH_3}{C_6H_3})\underset{CH_3\ (CH_3)_2}{C}\text{-}CH_2C(CH_3)_3\right]Cl\cdot H_2O$ | Pure monohydrate salt | 480 | |

### Miscellaneous Nitrogen Compounds

| | | | | | |
|---|---|---|---|---|---|
| sym-N,N'-Diphenylethylene-diamine | EK | $(C_6H_5)NHCH_2CH_2NH(C_6H_5)$ | Eastman Grade "White Label" | 212 | |
| Benzidine | EK | $NH_2(C_6H_4)\text{-}(C_6H_4)NH_2$ | Eastman Grade "White Label" | 184 | |
| Duomeen 12 | Ar | $CH_3(CH_2)_{11}NH(CH_2)_3NH_2$ | ~80% Diamine | 242 | 303[a] |
| Duomeen C | Ar | R-$NH(CH_2)_3NH_2$, straight-chain alkyls from coconut oil. | ~80% Diamine | 257 | 321[a] |
| Duomeen S | Ar | R-$NH(CH_2)_3NH_2$, straight-chain alkyls from soy bean oil. | ~80% Diamine | 321 | 402[a] |
| N,N,N',N'-Tetra(2-ethyl-hexyl)ethylenediamine | C | $\left[(C_4H_9\underset{C_2H_5}{\text{-}}CHCH_2)_2NCH_2\text{-}\right]_2$ | Laboratory sample | 509 | |
| N,N'-bis(α-methylbenzyl)-ethylenediamine | C | $(C_6H_5)\underset{CH_3}{C}HNHCH_2CH_2NHC\underset{CH_3}{H}(C_6H_5)$ | Laboratory sample | 266 | |
| Cetyldimethylamine oxide (Ammonyx Co.) | O | $CH_3(CH_2)_{15}\overset{\cdot\cdot}{\underset{O}{N}}(CH_3)_2$ | 20% Active | 286 | |
| 4-n-Amylpyridine | EK | $\overbrace{CH:CHN:CHCH:C}\text{-}(CH_2)_4CH_3$ | Practical grade | 149 | |
| 5-Ethyl-2-methylpiperidine | C | $\overbrace{CH_2\underset{C_2H_5}{C}H\ CH_2CH_2\underset{CH_3}{C}H\ NH}$ | | 127 | |
| Heptadecylglyoxalidine | C | $\overbrace{NHCH_2CH_2N:C}\text{-}(CH_2)_{16}CH_3$ | Laboratory sample | 309 | |
| 1-Hydroxyethyl-2-hepta-decenylglyoxalidine | C | $CH_3(CH_2)_7CH{:}CH(CH_2)_7\text{-}\overbrace{C:NCH_2CH_2}NCH_2CH_2OH$ | Laboratory sample | 351 | |
| Decahydroquinoline | EK | $\overbrace{CH_2CH_2CH_2CH_2CHCHNHCH_2CH_2CH_2}$ | Eastman Grade "White Label" | 139 | |
| Laurylmorpholine | Ar | $\overbrace{CH_2CH_2OCH_2CH_2N}(CH_2)_{11}CH_3$ | Laboratory sample | 255 | |
| N-N-dimethyl-p-toluidine | EK | $CH_3(C_6H_4)N(CH_3)_2$ | Eastman Grade "White Label" | 135 | |
| Amine C | A | $CH_3(CH_2)_n\text{-}\overbrace{C:NCH_2CH_2}N\text{-}R$, n = 10 | 85% Active | 276 | |
| Amine O | A | " " n = △16 | 85% Active | 355 | |
| Methyllaurylnitrosoamine | A | $CH_3(CH_2)_{11}\underset{CH_3}{N}\cdot N:O$ | Laboratory sample | 228 | |

(a) Molecular weight:
Where an indefinite formula or a mixture is listed, the "theoretical mol. wt." is an average value, either quoted by the vendor or calculated from the stated percent distribution of alkyls. The "apparent mol. wt." where marked (a) is an experimental value quoted by the vendor; where not so marked, it is a titration acid equivalent obtained in this laboratory.

(b) C, H, N % determined in this laboratory; other information principally as quoted by vendor.

(c) Laboratory sample of an amine, the name and formula not released for publication.

(d) Source of compounds:

| | | | |
|---|---|---|---|
| A | Alrose Chemical Co., Providence, R. I. | G | B. F. Goodrich Chemical Co., Cleveland |
| ADM | A. D. Mackay, Inc., New York | HD | Hilton-Davis Chemical Co., Cincinnati |
| Ar | Armour Chemical Div., Chicago | M | Monsanto Chemical Co., St. Louis |
| B | Bios Laboratories, New York | O | Onyx Oil and Chemical Co., Jersey City |
| C | Carbide & Carbon Chemicals Co., New York | RH | Rohm and Haas Co., Philadelphia |
| E | Edcan Laboratories, Norwalk, Conn. | S | Sterwin Chemicals, Inc., New York |
| EK | Eastman Kodak Co., Rochester, N. Y. | Sh | Sharples Chemicals, Inc., Philadelphia |

# APPENDIX B

## SYNTHESES

R. S. Lowrie

Since the variety of long chain secondary and tertiary amines available from commercial sources was limited, a number of these compounds were prepared at this laboratory. For the most part, all of the procedures used in this work were well detailed in the literature, although some modifications were occasionally developed for specific purposes. Only a general outline of the synthesis schemes followed are presented below. In preparing any specific compound, the actual starting point in this scheme was determined by the availability of the raw materials.

The basic starting materials were alcohols having the desired alkyl chains. These alcohols were first oxidized to aldehydes, ketones, or acids.[1] The acids were converted to nitriles,[1] then catalytically reduced to a mixture of primary, secondary and some tertiary amines;[2] the aldehydes and ketones were converted to amines either by catalytic reaction with ammonia and hydrogen[3] or by first making the oxime,[1] followed by catalytic hydrogenation.[4] All of the amines produced were purified by careful fractional vacuum distillation. Compositions and purity grade were established from carbon, hydrogen and nitrogen determinations and nonaqueous titrations.[5]

Symmetrical secondary and tertiary amines were produced by catalytically deammoniating the primary amine either under hydrogen pressure[2] or by refluxing with large amounts of Raney nickel catalyst for long periods of time.[6] In the latter procedure, a nitrogen stream was used to sweep out the ammonia formed and thus force the reaction toward completion. Both procedures gave secondary and tertiary amines, which were purified and checked as above.

Nonsymmetrical secondary and tertiary amines were produced either by the reductive alkylation of the appropriate amine under pressure or by refluxing the amine with the desired alkyl bromide in the presence of sodium carbonate.[7] The latter procedure was also used to produce symmetrical amines in some cases. Purification was accomplished and checked as above.

## References for Appendix B

1. Vogel, A. I., Practical Organic Chemistry, Longmans, Green and Company, 1951, Chapter 3, "Preparation and Reactions of Aliphatic Compounds."

2. The Chemistry of Fatty Amines, Armour Chemical Division, Armour and Company, Chicago, Ill., 1948.

3. Adams, R. A., et al., Organic Reactions, Vol. IV, John Wiley & Sons, Inc., 1948, Chapter 3, "The Preparation of Amines by Reductive Alkylation."

4. Winans, C. F., and Adkins, H., "The Preparation of Amines by Catalytic Hydrogenation of Derivatives of Aldehydes and Ketones," J. Am. Chem. Soc., 55, 2051 (1933).

5. Fritz, J. S., Acid-Base Titrations in Nonaqueous Solvents, G. Frederick Smith Chemical Company, Columbus, Ohio, 1952.

6. Hoerr, C. W., Harwood, H. J., and Ralston, A. W., "Solubilities of High Molecular Weight Symmetrical Normal Aliphatic Secondary Amines," J. Org. Chem., 9, 201 (1944).

7. Blicke, F. F., and Monroe, Ezra, "Antispasmodics I," J. Am. Chem. Soc., 61, 91 (1939).

# APPENDIX C

## MECHANISM OF EXTRACTION

Several points have been noted throughout this report which involved questions of extraction mechanism. Although the actual mechanism of uranium extraction and the exact constitution of the uranium species in the organic phase have not been established, relationships have been observed in the course of empirical extraction studies which provide some information on both points. In particular, there appears to be a close analogy between extraction with amines and sorption by (weak-base) anion exchange resins. In addition to the empirical testing program, studies of the physical chemistry of the extraction of acids and of uranium are in progress and will be reported later. Some preliminary results from these studies, with a minimum of experimental detail, are included in the following discussion.

The extraction of uranium from a sulfate solution can be represented by the following general equation

$$UO_2^{++}{}_{aq} + SO_4^{=}{}_{aq} + n(R_3NH)_2SO_4\,org \rightleftharpoons UO_2SO_4 \cdot n(R_3NH)_2SO_4\,org \quad (1)$$

which implies nothing about the nature of the bonding (i.e., type of compound) in the product, nor about the species in which the uranium may exist as it passes from the aqueous into the organic phase. This equation can then be modified to represent more specifically the various hypothetical species and mechanisms which may be considered.

The radical $(R_3NH)^+$ in Eqn. (1) represents the protonated amine, or alkylammonium ion, which is in equilibrium in acidic solutions with the free amine

$$2R_3N + H_2^{+}SO_4^{=} \rightleftharpoons (R_3NH)_2^{+}SO_4^{=} \quad (2)$$

(Similarly for secondary and primary amines, $R_2NH + H^+ \rightleftharpoons (R_2NH_2)^+$ and $RNH_2 + H^+ \rightleftharpoons (RNH_3)^+$.) More specifically, when the alkyl groups are sufficiently large to keep the amine and its salts in the organic phase in preference to water,

$$2R_3N_{org} + H_2^{+}SO_4^{=}{}_{aq} \rightleftharpoons (R_3NH)_2SO_4\,org \quad (3)$$

Study of this equilibrium with di-n-decylamine (0.1 and 0.01M, in benzene) showed that as the free amine was treated with increasing amounts of acid, nearly all of the amine was converted to the normal sulfate when the pH of the aqueous phase reached about 3. As the pH dropped still lower, some bisulfate began to be formed,

$$(R_3NH)_2SO_{4\,org} + H_2{}^+SO_4{}^=_{aq} \rightleftharpoons 2(R_3NH)HSO_{4\,org} \qquad (4)$$

less than half of the amine being in the bisulfate form at pH 1.

Equations (3) and (4) are similar to equations representing acid pickup by weak-base anion exchange resins. Further, one anion can be displaced by another.

$$(R_3NH)_2SO_{4\,org} + 2H^+NO_3{}^-_{aq} \rightleftharpoons 2(R_3NH)NO_{3\,org} + H_2{}^+SO_4{}^=_{aq} \qquad (5)$$

$$(R_3NH)_2SO_{4\,org} + 2Na^+OH^-_{aq} \rightleftharpoons 2(R_3NH)OH_{org} + Na_2{}^+SO_4{}^=_{aq} \qquad (6)$$

$$(R_3NH)OH_{org} \rightleftharpoons R_3N\cdot H_2O_{org} \rightleftharpoons R_3N_{org} + H_2O \qquad (7)$$

The equilibrium in Eqn. (5) lies to the right, i.e., sulfate was found to be more readily replaced by nitrate than nitrate by sulfate. This is in agreement with the order of affinities found with anion exchange resins.

The foregoing analogies suggest that the uranium extraction might involve an anion-exchange mechanism, and although it would be difficult to prove this to the exclusion of all other conceivable mechanisms, the anion-exchange concept has been useful in explaining and correlating the extraction and stripping results. As in describing anion-exchange with resins, it is convenient to assume that all complex formation takes place in the aqueous phase,

$$UO_2{}^{++} + xX^- \rightleftharpoons [UO_2X_X]^{-(x-2)} \qquad (8)$$

followed by simple exchange of anions,

$$[UO_2X_X]^{-(x-2)}_{aq} + (x-2)(R_3NH)X_{org} \rightleftharpoons [UO_2Xx](R_3NH)_{(x-2)org} + (x-2)X^-_{aq} \qquad (9)$$

These equilibria can account at least qualitatively for the impairment of uranium extraction as the sulfate concentration is increased (Section III E, Figure 4). Equation (1) would suggest that increased sulfate should aid the extraction, but Eqns. (8) and (9) show that there can be opposing effects: An excess of the anion aids in formation of the favorable anionic uranium complex, but it also competes for association with the amine. When X in Eqns. (8) and (9) represents sulfate (with due modification for the valence), it appears from the results in both amine extraction and anion-exchange resin sorption that a very small excess of sulfate forms a sufficient amount of the favorable complex for effective extraction, while a larger excess of sulfate only increases the competition.* With phosphate also, the competition appears to be the more important effect at moderate to high concentrations. Chloride and especially nitrate, on the other hand, do not permit good extraction unless the concentration of the anion is high. In terms of Equations (8) and (9), this is consistent with the less effective complexing of uranyl by chloride and nitrate in aqueous solution, only cationic or neutral species being formed at moderate concentrations. These results with phosphate, chloride, and nitrate solutions (Section III E) like those with sulfate, are in qualitative agreement with anion-exchange resin sorption.

The general equilibria of Eqns. (8) and (9), when read right to left, represent stripping reactions. Specifically for three important cases of stripping, i.e., by dilute hydrochloric acid, by sodium carbonate, and by sodium hydroxide (Section III H),

$$[UO_2(SO_4)_y](R_3NH)_{(2y-2)org} + 2yH^+Cl^-_{aq} \rightleftharpoons UO_2^{++}Cl_2^-{}_{aq} + yH_2^+SO_4^={}_{aq} + (2y-2)(R_3NH)Cl_{org} \qquad (10)$$

---

*The adverse effect of increased sulfate could alternatively be ascribed to formation of higher sulfate complexes with the assumption that those are less favorable for extraction.

$$[UO_2(SO_4)_y](R_3NH)_{(2y-2)org} + (2y+1)Na_2{}^+CO_3{}^=aq \rightleftharpoons$$
$$Na_4{}^+[UO_2(CO_3)_3]{}^{-4}aq + yNa_2{}^+SO_4{}^=aq$$
$$+ (2y-2)NaHCO_3\,aq + (2y-2)R_3N_{org} \qquad (11)$$

$$2[UO_2(SO_4)_y](R_3NH)_{(2y-2)org} + (4y+2)Na^+OH^-aq \rightleftharpoons$$
$$\underline{Na_2U_2O_7}ppt + 2yNa_2{}^+SO_4{}^=aq + (4y-1)H_2O$$
$$+ (4y-4)R_3N_{org} \qquad (12)$$

Reactions (10) and (11) correspond to stripping methods used with anion-exchange resins. Reaction (12) is not suitable with resins because of the additional solid phase, but it provides a particularly useful method for stripping the amine solutions.

Evidence has appeared in several types of tests suggesting that the amine salts dissolved in hydrocarbon diluents exist at constant activity, at least when in equilibrium with an aqueous phase which is near pH 1. These tests involved the effect of amine salt concentration on (1) the equilibrium between free amine and amine sulfate, (2) the extraction coefficient for uranium from sulfate solution, and (3) the loss of amine from an organic to an aqueous phase.

(1) The equilibrium between free amine and amine sulfate, as shown in Eqn. (3), would be expected to conform to the usual mass action expression

$$K_C = C_{AS} / C_A^2 C_H^2 C_{SO_4} \qquad (13)$$

where the subscripts AS and A represent the amine sulfate and the free amine. However, the data obtained with di-n-decylamine (0.1 or 0.01M) in benzene conformed better to the expression

$$K_C' = 1 / C_A^2 C_H^2 C_{SO_4} \qquad (14)$$

which is the form that Eqn. (13) would take if the actual concentration of the amine sulfate in the organic phase were constant, e.g., if it existed in a separate liquid

phase with composition independent of the amount of benzene present, instead of in true solution in the benzene.

If the amine salt does form a separate phase, it must be as a stable dispersion in the hydrocarbon diluent, since the organic solution has the appearance of homogeneity. A colloidal dispersion does not seem unlikely, perhaps with a micellar structure analogous to soap solutions. However, as the existence of a separate phase has not yet been proved, it would be better to state only that the experimental results indicate a constant activity of the amine sulfate in the organic phase, without assumptions about its actual concentration.

(2) The uranium extraction as shown in Eqn. (1) would be expected to conform to the mass action expression

$$K_c = C_{UAS} / C_U C_S C_{AS}^n \qquad (15)$$

where the subscripts U and UAS represent the uranyl ion in the aqueous phase and the uranium-amine-sulfate complex in the organic phase. From this equation, the volumetric extraction coefficient, $E_a^o = C_{UAS}/C_U$, is

$$E_a^o = K_c C_S C_{AS}^n ,$$

and when the sulfate concentration is held constant,

$$E_a^o = k C_{AS}^n \qquad (16)$$

The relationship actually found (Section III E), when the organic phase was far from saturation with uranium, was that the extraction coefficient was directly proportional to the amine concentration, $E_a^o = kC_{AS}$. This is consistent with Eqn. (16) if n = 1, if the amine sulfate exist in the organic phase as an n-fold polymer $[(R_3NH)_2SO_4]_n$, or if the amine sulfate together with the uranium-amine-sulfate complex exist as a separate phase instead of being in true solution in the hydrocarbon diluent.

The possible explanation that n = 1 appears to be eliminated by the results of the saturation loading tests (Section III G) which indicated a limiting ratio of one mole of uranium to about 5 or 6 moles of amine, i.e., to

about 3 moles of amine sulfate, n = 3. Furthermore, when the amount of amine sulfate remaining uncombined with uranium was estimated on the basis of n = 3, the relationship $E_a^o = kC_{AS}$ was found to hold well even when the organic phase approached saturation with uranium. (Here as elsewhere, $E_a^o$ and $C_{AS}$ are the nominal values of extraction coefficient and concentration, calculated on basis of the entire organic phase volume.) A clear-cut choice cannot as yet be made between the other two possible explanations, i.e., existence of the amine sulfate as an n-fold polymer or at constant activity, although the other evidence described above and below favors the latter.

(3) It was pointed out in Section III D that the amounts of several different amine salts lost by distribution to aqueous solutions were proportional to the volume of the aqueous phase rather than proportional to the nominal concentration of amine in the organic phase. Distribution behavior of this type could be due to the nature of either the aqueous or the organic phase, but in this case it appears more likely to be due to the organic. If the linear loss were ascribed to the nature of the aqueous phase, that is, if it simply represented saturation of the aqueous solution with amine salt, it would be further necessary to assume that this saturation level was reached when the amine concentration in the organic phase was quite low (0.005M in some tests), and also that the saturation level was sensitive to the composition of the very small amount of hydrocarbon diluent which also dissolved in the aqueous phase, since the quantities of amine differed considerably with benzene, Amsco D-95, and kerosene. The alternative explanation appears simpler and more probable, that the amine salt existed at constant activity in the organic phase, so that conformity to a simple distribution law gave directly a constant concentration in each aqueous liquor from each organic "solution."

Measurements of the freezing-point depression and the vapor pressure of the diluent, which are in progress, should give further information about the amine activity in the organic phase. Meanwhile, since the three types of evidence described provide essentially independent indications of the amine salt activity, the following tentative generalization seems justified: The mineral-acid salts formed at pH 1 with amines in the molecular weight range which is useful for liquid-liquid extraction appear to exist in hydrocarbon diluents at constant activity, probably as colloidal dispersions, over a considerable range of nominal concentrations.